Ultra clean combustion, oxycombustion of hydrogen

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Abstract

When the renewables energy technologies are producing additional power, then they require a medium to store it. An optimal solution to this problem seems to be hydrogen, which role will be significant in emerging technologies of the future. The paper presents a concept of oxy combustion of hydrogen, which has too high combustion temperature for typical gas turbines. Hence, it is important to develop reliable gas turbines which allow fuel flexibility and low emissions. Calculations to analyse the chemical kinetics are conducted using the Cantera Software. In the result is it possible to combust hydrogen completely in oxygen/steam mixtures. The systems were investigated under various sets of temperature and pressure in the result the residence times and volumes of the reactors, such that complete combustion is achieved are presented.

Key words: combustion; hydrogen; chemical kinetics; oxycombustion of hydrogen; reactor modelling

Resumo

Quando as tecnologias de energia renovável produzem energia em excesso, é necessário um meio de armazenamento. Uma solução ideal para este problema parece ser o hidrogénio, que terá um papel significativo para as tecnologias emergentes do futuro. Esta tese apresenta um conceito de oxicombustão hidrogénio, que tem temperatura de combustão muito alta para turbinas a gás típicas. Por isso, é importante desenvolver turbinas a gás confiáveis que permitam flexibilidade de combustível e baixas emissões. Os cálculos para analisar a cinética química são realizados usando o software Cantera. Em resultado, é possível queimar completamente o hidrogénio em misturas de oxigénio / vapor. Os sistemas foram investigados sob várias condições de temperatura e pressão, resultantes do tempo de residência e do volume de residência dos reatores, de tal maneira que a combustão completa seja alcançada.

Palavras-chave: combustão; hidrogénio; cinética química; oxicombustão de hidrogénio; modelagem de reatores

Table of contents

List of figures

List of tables

Nomenclature

LATIN

A	Pre-exponential factor
A_s	Chemical formula of species
$[A], [B], [C]...$	Mole concentration, kmol/m^3
c_i	Concentration of species i, kmol/m^3
c_p	Specific heat, J/Kkg
c_s	Concentration of species s, kmol/m^3
(e)	Reactant species
E_a	Activation energy, kJ/mol
h	Enthalpy, J
h_{in}	Enthalpy at the inlet, J
h_k	Enthalpy for species k, J
K_c	Equilibrium constant
k_b	Reaction rate of backward reaction
k_f	Reaction rate of forward reaction
k_r	Reaction rate of reaction r
LHV	Lower Heating Value, MJ/kg
$\dot{m}$	Mass flow rate, kg/s
$\dot{m}_{in}$	Mass flow rate at the inlet, kg/s
$\dot{m}_{out}$	Mass flow rate at the outlet, kg/s
m	Mass, kg
(p)	Product species

p	Pressure, bar
P	Produced power, MW
R	Universal gas constant, J/molK
S	Entropy, J/K
tr	Residence time, s
t	Time, s
T	Temperature, K
T^*	Temperature at the enter, K
V	Volume, m^3
v_{rs}	Stochiometric coefficients of the reactants
W_k	Molecular weight, kg/kmol
Y_k	Mass fraction composition, %
Y_k^*	Mass fraction composition at the enter, %

GREEK SYMBOLS

B	Temperature modifier exponent
ρ	Density, kg/m^3
$\dot{\omega}_k$	Molar reaction rate of species k, $kmol/m^3s$

INDICES

ppm	parts per million
ppmvd	parts per million, volumetric dry

ABBREVATIONS

CC	Combustion Chamber
CDC	Colorless Distributed Combustion

CFD	Computational Fluid Dynamics
CSTR	Continuously Stirred Tank Reactor
DLN	Dry Low NOx
DOE	Department of Energy
ENEL	Ente Nazionale per l'Energia Elettrica
FLOX	Flameless Oxidation
GE	General Electric
HiTAC	High Preheated Air Combustion
HPT	High Pressure Turbine
HRSG	Heat Recovery Steam Regenerator
LHV	Lower Heating Value
LPT	Low Pressure Turbine
MILD	Moderate or Intense Low Oxygen Dilution
MNRC	Modified New Rankine Cycle
MPT	Medium Pressure Turbine
NTP	Normal Temperature and Pressure
OXY	Oxygen
PSR	Perfectly Stirred Reactor
RANS	Reynold Averaged Navier-Stokes
TG	Gas Turbine
TP	Temperature and Pressure
US	United States
WSR	Well-Stirred Reactor

1 OVERVIEW

In the past decades the demand for primary energy was increasing with a dramatic rate because of the economical and technological development as well as population growth [1]. The energy consumption increases with economical development because the production and consumption need energy as a basic input. The increasing hunger for energy affects other fields like politics, environment and economy. Although the renewables sources of energy (wind, solar, geothermal, biomass) [1] are developing and play more and more important role already but the process of energy production from combustion of fossil fuels is dominating and is still needed to cover the rapid growth of energy consumption of developing countries. The known and applied methods of combustion raise worldwide attention because their negative effect on the environment due to emission of hazardous gases and particulate matter. Moreover, the fossil fuels sources are nearly exhausted and there is a need to find a substitution for this source of energy. The consequences of decades-long combustion of the fossil fuels like air pollution, global warming, acid precipitations, oils spills, etc. can be observed nowadays. The world is facing a challenge of overcoming these changes and redirecting the global development to low-carbon economy. Therefore, new carbon-free energy carriers need to be introduced and new technologies of their utilization need to be developed. Furthermore, the energy storage systems are required. Since many of such technologies are already known (e.g. fuel cells, electrolysers, batteries, etc.), their economical competitiveness and energy effectiveness need to be improved to make them broadly available.

In the present thesis, the concept of oxy combustion of hydrogen is presented and studied. Hydrogen is the energy carrier, fuel and raw material. Whenever it is produced with the usage of renewable sources that it could contribute to decreasing of the emissivity of greenhouse gases, increasing the energy independence and mitigating the challenges related to the unstable production from renewable energy systems. Hydrogen is considered as the key element of energy and transportation systems of the future. Many national research groups are developing the hydrogen production methods, delivery, storage and conversion technologies. The final utilization of hydrogen takes place in the fields of industry, energy and transportation.

2 MOTIVATION AND CONTENTS

The main objective of the thesis is to analyze the process of hydrogen combustion in oxygen diluted with steam. The reason for this study is twofold:

- new concept steam cycles have been proposed in the literature [2] that allow for efficient utilization of hydrogen and production of electricity in a zero-emission system
- dilution of oxygen with steam allows to overcome the cooling problem of high temperature non-premixed H_2-O_2 flames

Therefore, the purpose is also to understand the parameters allowing for stable and complete combustion of hydrogen in diluted oxygen. The aim is realized by numerical modelling by means of chemical kinetics software Cantera [3]. First the important thermodynamic parameters (temperature, gas composition, pressures) are examined with the assumption of equilibrium. In the second stage a perfectly stirred reactor (PSR) model is used to study the effect of the residence time. Finally, the influence of the reactor volumes and residence times on ignition and reactions completeness was studied. The calculations on given topic have been made and set of the results is presented and discussed in the thesis.

The thesis contains six chapters. In the first chapter the brief introduction about hydrogen is given, then the objectives of the conducted study are explained. State of the Art chapter focuses on the theoretical information given in the previous studies and literature in this relevant topic. In the chapter about computational model the techniques and governing equations which are used in the simulation software are presented. In the fifth chapter the results of computations are given with a discussion. The last chapter includes conclusions about the study.

3 STATE OF ART

In this chapter, a literature review of associated topics is conducted in order to provide better understanding of the discussed topic. The hydrogen properties and combustion characteristics are presented and the methods of hydrogen production. Modern appliances used in production of electricity from burning gases is showed and two type of combustion methods are described, namely premixed and non-premixed combustion. The type of combustion technique, applicable in hydrogen combustion is reviewed, namely MILD-OXY combustion.

3.1 Properties and Combustion Characteristics of Hydrogen

Elemental hydrogen is the smallest chemical element because it is constituted by only one proton and one electron. Hydrogen is also the most common element in the universe, and it takes the third place on Earth. It was discovered by the English chemist and physicist Henry Cavendish in eighteen century, he proved that hydrogen is a compound of water particle. On the other hand, it is said that many chemists, during their experiments, discovered it years before and named it as the “flammable gas”. Hydrogen has three isotopes, which shows various physical properties but similar chemical properties. Due to atomic mass of this element it is 14.5 times lighter than air.

Although, as it was said, elemental hydrogen is simple and common on the Earth, it exists in molecular form H_2 in extremely small amount of 1%. [4] At standard conditions of temperature and pressure this diatomic gas is nontoxic, nonmetallic, odorless, tasteless, colorless and is highly combustible. The small size of molecules results also in occurrence of spontaneous reaction with oxidizing elements. The hydrogen bonded with oxygen forms water, which is not combustible, but when it is bonded to carbon it creates a hydrocarbon which reacts rapidly with oxygen, producing heat, carbon dioxide (or/and monoxide) and water vapor.

Table 1 Comparison of properties of hydrogen and two other gaseous fuels [4,5].

		Hydrogen	*Methane*	*Propane*
Molecular weight	g/mol	2.016	16.04	44.097
Boiling point	K	20.3	111.7	230.8
Gas density at NTP	kg/m^3	0.0899	0.718	2.01
Self-ignition temperature	K	845–858	813–905	760–766
Minimum ignition energy	mJ	0.02	0.3	0.25
Flammability range in air	vol %	4–75	5–15	2–10
Flammability range	Φ	0.1–7.1	0.4-1.6	0.56–2.7
Stoichiometric composition in air	vol %	29.53	9.48	4.02
Diffusivity in air	cm^2/s	0.63	0.2	0.1
Adiabatic flame temperature	K	2318-2400	2158–2226	2198–2267
Burning velocity	cm/s	237	42	46
Lower heating value	MJ/kg	118.8–120.3	50	46.35
Higher heating value	MJ/kg	141.75	55.5	-
Lower heating value	MJ/m^3	10.78	35.8	91.21
Higher heating value	MJ/m^3	12.75	39.72	99.03
Lower Wobbe index	MJ/m^3	40.7	47.94	73.3

NTP=normal temperature (273.15K) and pressure (101.325kPa)
Figures of heating values can vary dependent on source

Hydrogen is considered to be a significantly hazardous compound in comparison to other fuels, for example methane and propane. Hydrogen is highly volatile, due to its low density. Moreover, it is characterized by small size of molecules and it can diffuse through many materials like polymers, rubbers and different metal alloys. Due to this high coefficient of diffusivity in air, it results in high flame velocity. The flammability range of hydrogen in air is very wide and the mixture of those two compounds is highly explosive. Hydrogen has the greatest lower and higher heating values among fuels, in reference to mass and very small in reference to normal volume.

A detailed review through past and present research and development in the topic of combustion of hydrogen and hydrogen fuel mixtures can be found e.g. in [4-6]. In those literature sources, the impact of H_2 on the lower and higher heating values, flame velocity, laminar and turbulent burning velocities, adiabatic flame temperature, flammability range in air, flashback, blow-off, auto-ignition, ignition delays and emissions were collected and presented. Some of those properties still need a lot of research work done especially for fuel mixtures with higher hydrogen content and fuel mixtures with other fuels, such as CH_4, CO , biogas, etc. Many typical characteristics of H_2 make this fuel a unique source of energy, which still needs to be well known and trained. Consequently, researchers point out several issues, such as significantly different thermochemical and transport properties of hydrogen in comparison to well-known hydrocarbon fuels, which needs execution of basis experiments for better knowledge. An example of this can be thermal and momentum diffusivities of hydrogen, which is around six times higher, and mass diffusivity 3 times higher than methane. The diffusion process in the flame is a consequence of those differences. As it is shown in table 1, the level of adiabatic flame temperature is around 150K higher when compared to CH_4 and C_3H_8 with the same stoichiometry. The result of increased adiabatic flame temperature is an increased NO_x emission, which means in fuel mixtures with higher hydrogen content production of NO is believed to be higher. The maximum temperature in the combustor depends on the adiabatic flame temperature, which affects the efficiency and also the type of material used for production of the combustor. The outcome of higher adiabatic flame temperature can be on one hand increased efficiency, but the drawback of this is the possibility of overheating of combustor. The higher flame speeds of hydrogen, which is 6 time higher than methane, is the consequence of higher reactivity. All of this could be a reason for occurrence of flashback in premixed burners. From one study conducted [4] one can say that even a small fraction of methane can lower the risk of flashback significantly. The wide range of flammability of hydrogen is also the result of the high reactivity. Thanks to these broadening limits of leaner combustion of hydrogen fuel mixtures is possible, which shows the possibility of improvement of emission and efficiency. On the other hand, there is lack of data for fully understanding hydrogen’s upper flammability limit at various temperatures, pressures and composition of fuels.

The influence of hydrogen addition to the fuel mixture can present the following drawbacks:

- Possibility of occurrence of flashback
- Possibility of self-ignition during mixing
- Risk of lack of stability
- Increasing moisture fraction in hot gas path
- Decreasing energy per unit volume

The fuel composite with hydrogen addition presents also some potential advantages:

- Increasing energy per unit mass
- Decreasing blowout limit
- Decreasing CO emission
- Decreasing flame temperature
- Decreasing NO_x emission

Although a large number of studies have been performed to examine hydrogen containing fuels the literature on this topic is still limited. All mentioned factors are the proof that knowledge of the basic properties is important in the case of progress in development of hydrogen based technologies. While all experiments are undertaken it is also worth to mention that properties and common interactions of species in the H_2-O_2-H_2O mixture should be considered. During developing of hydrogen applications, a very important factor is assurance of safety, which in some cases cannot be possible, because detection methods shows not adequate measurements.

3.2 Methods of hydrogen production

Hydrogen is a promising energy carrier which could replace current sources, but easy, cheap and efficient way of production needs to be developed. Nowadays 95% of hydrogen production processes are based on wood or natural gas or oil. The most popular methods of hydrogen production are: [7]

- Steam methane reforming

The most popular one is the method of steam methane reforming. In this process natural gas is transformed into synthesis gas, important raw material in further processes, which contains hydrogen and carbon monoxide. Conversion of methane is possible with usage of water/steam, oxygen and carbon dioxide. There are three methods of reforming: steam reforming, two-stage reforming and autothermal reforming.

In the first method, heat is supplied to the system and reaction takes place on a nickel catalyst with a usage of steam as a converting agent. In the second method, process is realized in two stages, first one is similar to steam reforming from first method and in the second stage unreformed methane is subjected to afterburning. Heat used in second stage comes from first stage. In the third method, two stages are carried out at the same time, partial combustion of methane and steam-oxygen conversion. In purpose to obtain pure hydrogen, synthesis gas needs to be processed, to remove CO by conversion it into CO_2 by water-gas shift. This process is usually carried out in two stages: high temperature (400 °C, the catalyst is a $Fe - Cr$) and low temperature (220 °C, the catalyst Cu). Next, CO residues are removed in the methanation process (at 320 °C on a nickel catalyst, the conversion from CO to CH_4). Finally, pure hydrogen is obtained after the absorption of CO_2 in activated K_2CO_3in solution of KOH.

Reaction of steam-methane reforming:

$$CH_4 + H_2O + heat \rightarrow CO + 3H_2$$

Water-gas shift reaction:

$$CO + H_2O + heat \rightarrow CO_2 + H_2$$

- Gasification

Fossil fuels for example coal or biomass consists mainly of carbon and water, which are burned in a reactor at very high temperatures around 1200 °C and 1500 °C. During reaction releases gas which later reforms in order of production of hydrogen and carbon monoxide. This technology is very profitable in coal rich countries, for example China and South Africa. For large-scale hydrogen production there are steam gas generators.

Gasification:

$$C + H_2O \rightarrow CO + H_2$$

- Plasma reforming

Modern technological processes based on electricity, which is an unfortunate disadvantage, enable H2 production with nearly no CO2 emissions. This method was developed in eighties by a Norwegian company and it made possible the separation of hydrocarbons into hydrogen and pure carbon at 1600°C.

In the United States there is ongoing research on the construction of a plasma reformer. The advantage of such a reformer is that it is suitable to produce hydrogen from various hydrocarbon substances, including heavy oil fractions. Furthermore, it is suitable for pyrolysis - thermal decomposition process of the heavy fraction of organic material, without air and oxygen. The US reformer is operated at a temperature of 2000 °C, in range of 80-90% hydrogen.

- Electrolysis of water

The most interesting and easy method of production of hydrogen is through electrolysis of water. In this procedure water is split into hydrogen and oxygen using electricity. When sources of this electricity are renewable, the entire process is emission free. Hydrogen is released on the negative electrode: anode, and oxygen on the positive electrode: cathode. With usage of ion separator gases can be kept in separate containers. A 25% potassium hydroxide solution is added to the water in order to increase the electrical conductivity of the electrolyte.

The overall reaction of water decomposition under the influence of a constant electric current is the following:

$$2H_2O \rightarrow 2H_2 + O_2$$

Anode reaction:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

Cathode reaction:

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$

There are under development pressurized structures of compact electrolysers, useful to produce hydrogen at a pressure of 30 atmospheres, at petrol stations. Another type of device is the so-called steam cell, in which the electrolyte is in the form of a ceramic ion conductor. It has high performance but is not yet available for purchase. This method of producing hydrogen can be profitable almost exclusively for countries with cheap electricity, mainly from hydropower plants, such as Norway, Iceland.

- Photo electrolysis

This is a way of conversion solar energy into hydrogen. In this method sunlight is used by a photoelectrochemical cell, submerged in water, which separates the water into hydrogen and oxygen bubbles. Photoelectrochemical cell is a combination of a photoelectric cell with a catalyst and it acts like an electrolyser. This method is a promising option in the criterion of commercialization. Another advantage are the savings in terms of production of electrolyser and increased productivity.

- Biogas gasification

Hydrogen can also be produced from biomass which is a renewable energy carrier. The process of gasification is similar to reforming of methane and other hydrocarbons. In the presence of high temperature, gas is obtained from biomass and then, in the next stage, the gas decomposes in presence of steam. The greenhouse effect of carbon dioxide, which is a by-product of those reactions, can be ignored because the carbon dioxide can be treated as neutral, in fact the plants from which biomass is obtained, will absorb the carbon dioxide in the following year.

- Biological methods

In many various biological processes, hydrogen is produced freely either directly or as a by-product. The example of biological methods can be the process of photosynthesis by green algae or the process of fermentation by microorganisms.

3.3 Premixed and non-premixed combustion

Combustion is a type of exothermic chemical reaction between fuel and oxidant. A commonly available oxidant is oxygen in the air. During this process heat and light are released. Taken into consideration a way of mixing fuel with air, two methods can be distinguished:

- Non-premixed
- Premixed

Non-premixed combustion is also called diffusive combustion and is used in most common technical cases. Fuel and oxidizer in this method are not mixed prior to combustion, reaction occurs simultaneously with the mixture formation process. The velocity of bringing reactants to the reaction zone is highly important. Fuel entering the reaction zone can be diluted with other gases. The desired proportions of fuel and oxidizer are stochiometric proportions, all reactions can occur only when all reactants are perfectly mixed. Reaction zone in this type of combustion is stable, it is not moving towards fuel stream or oxygen stream because of lack of a second reactant in that area. The advantage of non-premixed combustion is the safety of operation, since the flame does not propagate and does not auto ignite in undesired locations. Moreover, non-premixed combustion systems have simpler design of the burner, compared to premixed combustors. On the other hand, the disadvantage is lower efficiency, because mixing of fuel and oxidizer decreases velocity of chemical reactions. As shown on the figure below mean flame area is created from reacting species entrained by oxidizer - [8].

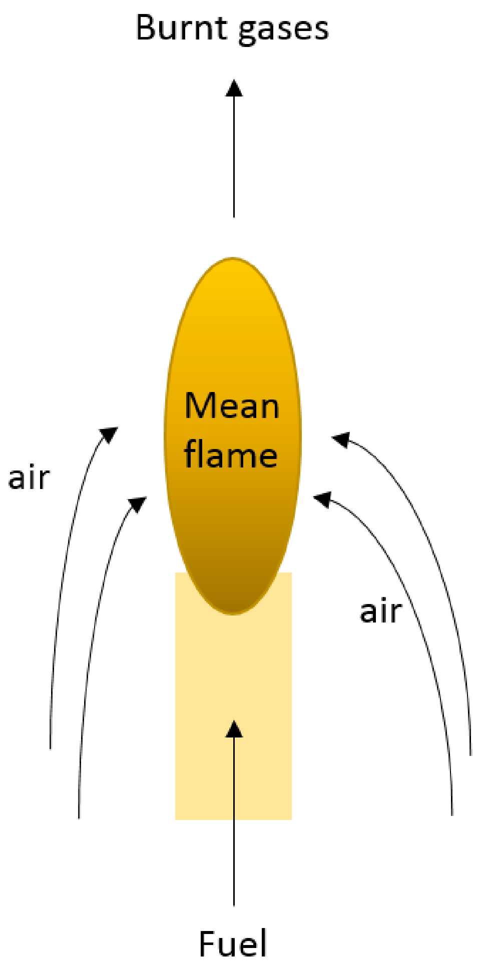

Figure 1 Schematic diagram of non-premixed flame (based on [8]).

Non-premixed flames fronts do not have any characteristic velocity. In this case there exist an intense chemical reaction zone exist, which in this method is hard to stop because of the combustion processes. Typical diffusion combustion occurs in liquid propellant rocket engines or Diesel engine. The simplest example of this type of burning is a candle flame, because thanks to free convection air moves in the direction of the flame. Non-premixed flames are in most cases much cooler than premixed flames due to the step of mixing fuel with oxidizer which results in limitation of combustion.

Premixed combustion is described as the combustion process in which from the beginning oxidizer is mixed with fuel or other combustible material in in gaseous form, filling the given volume. The supplied heat ignites the whole mixture at almost the same time, this is called an explosion. The typical premixed flame is characterized by the propagation of a wave flame. Two types of combustion waves can be distinguished: detonation wave (high velocity wave, with ongoing combustion), deflagration wave (low velocity wave, no occurance of pressure difference across the flame). In a premixed flame where the amount of oxidizer is not enough, in an outer zone of flame diffusion flame (figure 2) is created. In this zone products of partial oxidation are afterburn, for example carbon monoxide. The typical device for generation of premixed flame is the Bunsen burner showed on the figure below - [9].

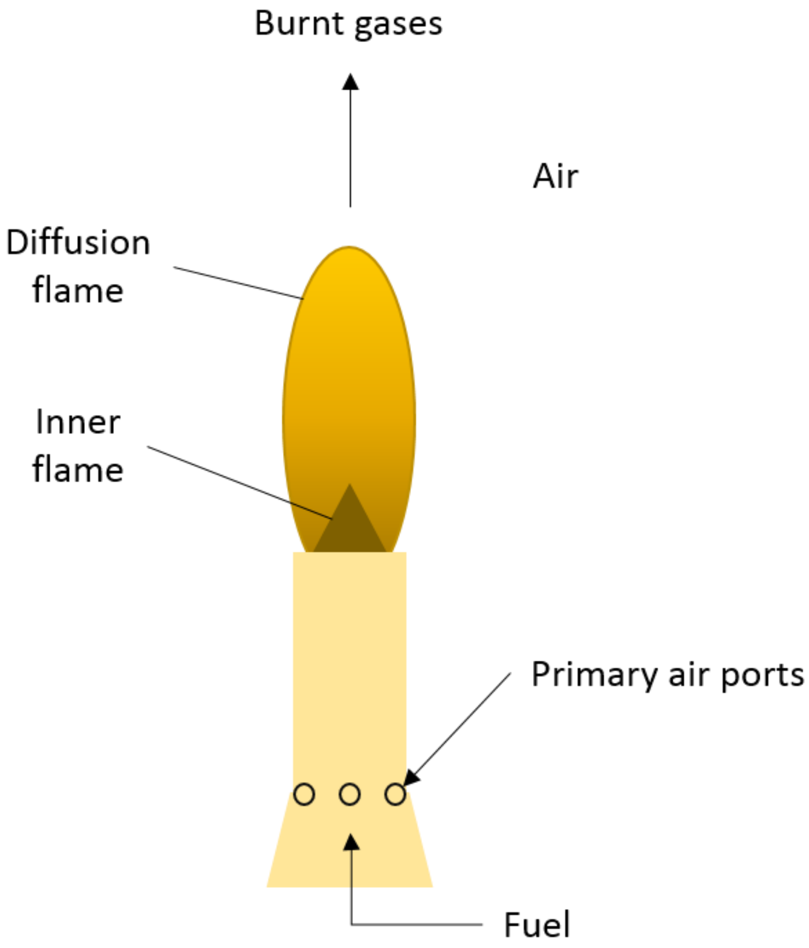

Figure 2 Schematic diagram of premixed flame (based on [9]).

At the bottom of the burner fuel mixes with the oxidizer, then this mixture moves upwards through a tube. When the mixture reaches top of the tube, it starts burning. The Bunsen burner is structured from two flames, the inner flame rich in fuel and the outer flame, diffusion flame.

Premixed combustion is mostly used in small devices, where the time of residence is low and high heat release rate is requested. This type of combustion can be lean combustion, which does not emit smoke and emits a small aomunt of nitrogen oxides. On the other hand, the posibility of explosions exists and all process is relatively unstable. The premixed flame front propagates spontaneously and its surface is not constant.. Essential in the design of premixed burner is determination of challenging parameteres like flashback and blow-off limit, flammability limit, auto-ignition, extinction and already mentioned stability of flame. Premixed combustion is relatively easy to stop.

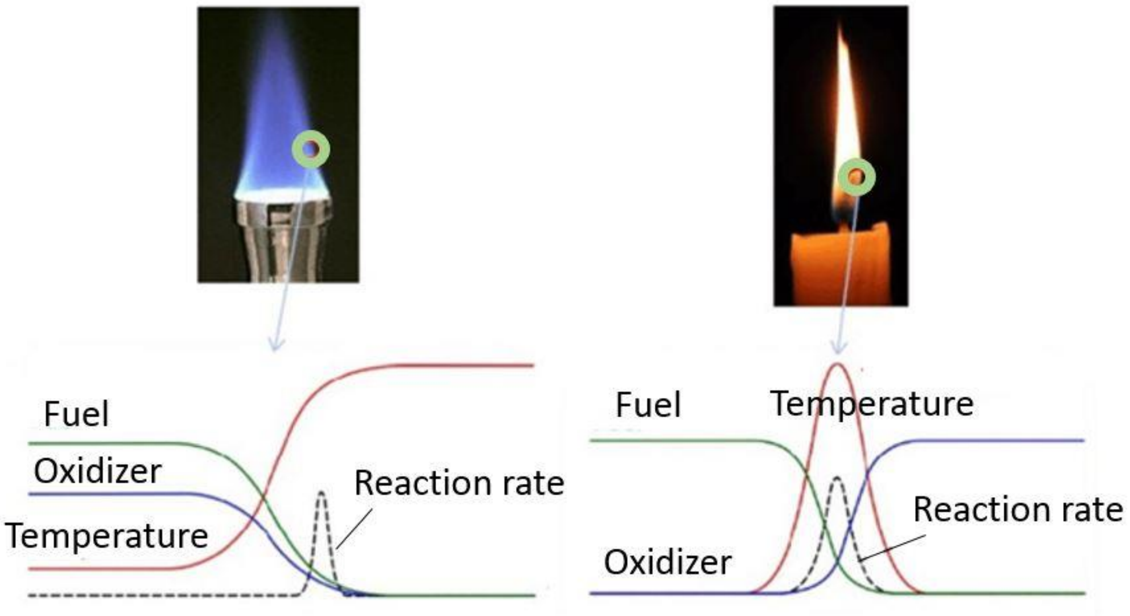

Figure 3 Concentration of fuel and oxidizer and temperature profile in premixed (on the left hand side) and non-premixed (on the right hand side) flame (based on [10]).

Figure 3 [10] showed above presents two different profiles of premixed and non-premixed type of combustion. In the premixed concept, where fuel and oxidizer are mixed before chemical reaction, the mixture of reactants is preheated first, which is connected with heat released, and temperature is slowly growing. In the next step there is a peak of reaction rate and fuel is totally burned. In another concept, where reaction appears on the boundary of fuel and oxidizer, heat is released at the same time as mixing of reactants occurs. The peak of temperature and reaction rate is at the same location at which nearly all fuel is combined with oxidizer.

Hydrogen-rich gases have specific effects on both premixed and non-premixed gas turbine combustion. There exist a couple of possibilities for usage of those type of combustion turbine designs, but they still need development. Global companies are targeting in rapid development of premixed based designs of gas turbines burning syngas or hydrogen.

An example of recently developed premixed gas turbine running on natural gas presents successful reduction in emission of NO_x to the atmosphere. The systems operating on lean premixed combustion can achieve nitrogen oxides emissions at the level lower than 25 ppm and in some cases even 10 ppm with negligible consequences of drop of cycle efficiency [6]. Drawback of premixed combustion can be lack of stability of the flame which causes problems with operability, increased emission of carbon monoxide, lack of safety of the system under operation.

In non-premixed methods of combustion lowering of nitrogen oxide level is not so simple but, there are more complicated ways to achieve this reduction in emission. One of the techniques can be using inert gas dilution, fuel staging or cleaning-up exhaust gases from NO_x particles. The first of those techniques, inert gas dilution, has much higher operating costs and higher efficiency penalty than the lean premixed combustion. This technique depends on dilution of the fuel with steam or nitrogen. In integrated gasification combined cycle dilution with nitrogen is preferable, because it results in smaller efficiency penalties. Application of diffusion combustors allows for avoiding problems related to premixed combustors such as self-ignition, flashback, blowout and lack of stability (due to acoustic pressure fluctuations coupled with heat release).

Hydrogen rich fuels have low a heating value compared to natural gas, from table 1 hydrogen is around 11 MJ/m^3 and methane is around 36 MJ/m^3. This difference may require changes in typical turbomachinery used for burning of natural gas, specially the compressor and fuel injectors design, in order to accommodate higher hydrogen flow rate. In the gas turbine, auto-ignition is an undesired property of combustion, in case of burning hydrogen it raises special anxiety. Whenever the residence time, of mixture of fuel and air, inside the premixer is longer than ignition delay time (usually 1-5 ms), that undesired ignition may occur [6]. There is still not enough data concerning this topic and consequence of this action can be harmful on hardware. Many authors argue about the safety of using premixed combustors for burning fuels containing hydrogen. Another topic of concern is blow out, studies about the hydrogen content in the fuel mixture says that increased hydrogen content can lower the equivalence ratio of which extinction of lean blow out flame can happen. Zhang [6] concluded in his studies that changes of hydrogen content in fuel from 0% to 80% decrease the equivalence ratio at blowout from 0.46 to 0.30 at temperature equal to 580K. In the premixed hydrogen combustors may occur flashback because of unstable operations which is result of very high flame velocity. High gas speed makes also challenging the design of combustor with pressure drop. To avoid those problems with premixed combustion, some researchers propose burning mixture of hydrogen and nitrogen, swirl premixers, lean direct injection or micromixers [11].

Environmental regulations force out keeping levels of emission of pollutants from gas turbines at specified standards. One of the key pollutants emitted in combustion in gas turbines is NO_x, which is responsible for generation of smog and contribute to occurrence of acid rain. To the group of nitrogen oxides include nitric monoxide (NO), nitric dioxide (NO_2) and nitrous oxide (N_2O). In a purpose of limitation of emission of nitrogen there can be two methods proposed premixed lean combustion or non-premixed combustion with dilution of a flame. The level of nitrogen oxides at the end of premixed combustion can differ depending on three main criteria: peak temperature, temperature distribution in burner, efficiency of premixing level. Burning fuel containing hydrogen can be seen as a solution of reduction of NO_x emission.

Possibilities of adjusting natural gas turbine for using hydrogen as a fuel was presented in Ref. [11]. In this study 50-Hz F-class large-scale plant was used, composed of one gas turbine, triple pressure level and reheat recovery steam generator. The layout applied in the mentioned paper is presented below [11]. In the top part of figure 4 there are three cases considered in the article:

a) Premixed flame combustor
b) Diffusive flame combustor with nitrogen dilution
c) Diffusive flame combustor with steam dilution

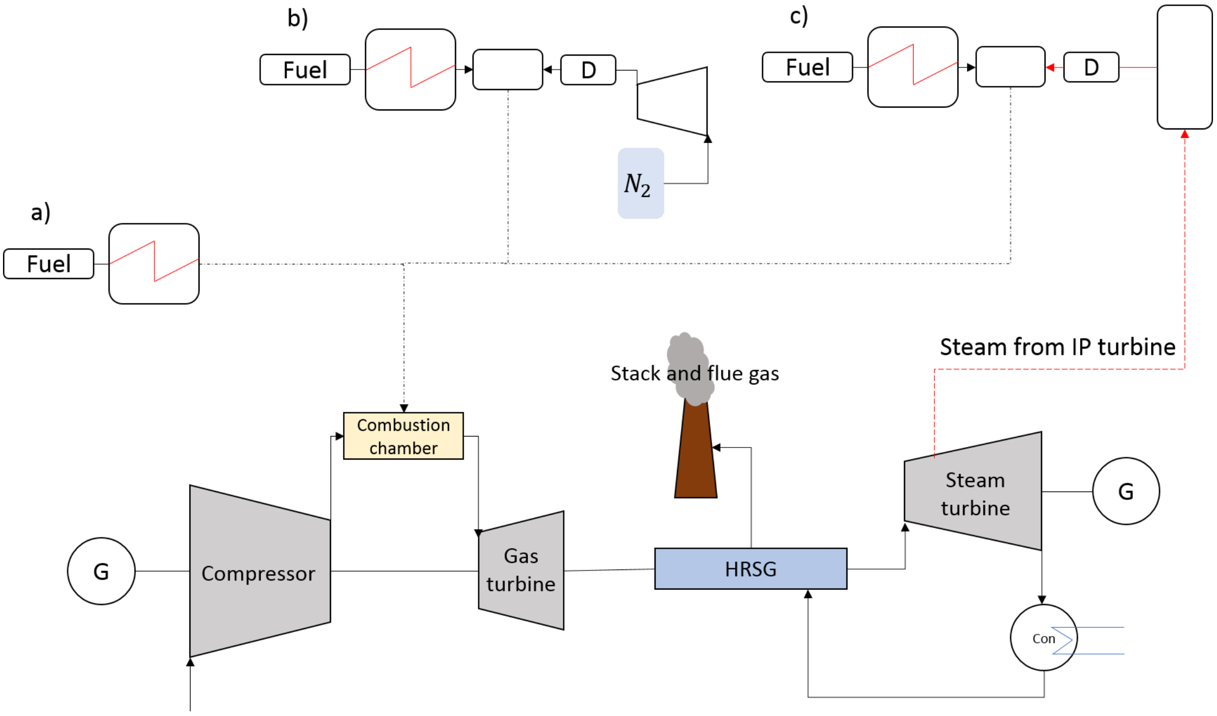

Figure 4 Diagram of hydrogen-fueled possibilities in combined-cycle plant (based on [11]).

Three parameters where checked in those studies such as: turbine inlet temperature, electrical efficiency of turbomachinery, maximal blade-metal temperature. Authors concluded that in comparison between those two diffusive flames with this same stochiometric temperature the case with nitrogen dilution presents higher electric efficiency than steam dilution. Comparing the premixed and diffusive combustor shows that better performance achieves by the first one. Considering metal blade temperature premixed combustor has higher performance.

Hydrogen-rich fuels have higher velocity of burning than natural gas (5.6 times larger flame velocity in stochiometric air). The composition of the synthetic fuels can vary from each other, and the gas turbines operating on this fuel type is diffusive gas turbine. The premixed combustors carry with them issues like flashback, blowout, self-ignition and lack of stability. Moreover, the techniques of reduction on nitrogen oxides are less efficient and more expensive. In addition, the diffusive flames do not propagate, they burn in the combustion region when fuel and oxidizer are implemented inside. Non-premixed combustion is applied in purpose of avoiding instabilities of flame and hazardous operation. Considering burning of pure hydrogen in presence of oxygen the problem with nitrogen oxides does not exist, therefore logical choice of burner in this type of project is non-premixed combustor.

3.4 Contemporary Gas Turbines

Society nowadays faces huge problems of coping together increasing demand for energy supply and on the other hand need of decarbonization. Hydrogen can play a role of storage medium of power from renewable energies produced by wind turbines or solar panels. When the electricity demand increased stored gas can be burned in specially dedicated gas turbines for production of electricity and heat and this type of thermal power generation does not rely on the weather. Many companies and organization all over the world are putting a lot of effort on the development of new more efficient technologies which will be at the same time less harmful to environment and production of carbon dioxide would be equal to zero. Already developed technologies of burning fuel mixtures with low share of hydrogen are allowed to be used in existing power generation plants.

Gas turbine is a type of engine which draws energy from the flow of flue gases which are the outcome of burning fuel in the presence of compressed air in the combustion chamber. A gas turbine power plant is composed of a compressor which is connected to a turbine by a shaft and a combustion chamber. Different types of fuel can be used in gas turbines and the most popular is natural gas but following the decarbonization trend in this field forces usage of other types of fuel, for instance hydrogen gas. In the case of using hydrogen as a fuel, the high combustion temperature of the gases at the outlet (with temperature around 900 ℃) can be reused as pre-heating agent of air at the entrance of the combustion chamber.

Typical gas turbine combustors which are nowadays in use for burning low-calorific gases are working in diffusion mode, this means that fuel is mixed with air in the combustion chamber and not earlier. This type of mixing on synthesis gas differs from typical operation with natural gas which is premixed with air before entering the combustion chamber. There is a need to follow nitrogen oxides level restrictions, that is why temperature is reduced because of hydrogen and water addition. Is a consequence, of the efficiency of turbines where fuel and air are mixed in the combustor will be reduced, compared to pre-mixing system. The progress in research over upgraded pre-mixing combustion system gives a chance for growth of inlet temperature of the turbine and growth of efficiency, compared to diffusion type combustion chambers. Inlet temperature is predicted to be around 150 °C higher, it will reach 1400 °C and this leads to an increase of efficiency of around 2%, according to the prediction of experts. [12] It is also assumed that the new system operating on hydrogen fuel will produce less than 15 ppm of NO_x with minimal dilution, by water or additional nitrogen from air separation. Decreasing the level of nitrogen oxides create additional costs of operation which have to be minimized but undertaken in order to overcome the challenge of hydrogen fueled gas turbines with low emissions, stable operation with dilution as simple as possible and as an outcome increased volumetric flows and reactivity, which can be compared to natural gas fueled turbines.

Higher than 30% volume of hydrogen in the fuel mixture is the obstacle in the usage of existing gas turbines, due to the problem of are flashbacks, increase of concentration of nitrogen oxides, combustion pressure differences, high temperature inside combustor (up to 1600 ℃). For instance, fuel nozzles could be drastically damaged because of risk of flashback. The result of those problems is the incapability of usage of traditional burners, even after basic modification. For burning pure hydrogen there is a request for totally new design from the grounds of the gas turbine combustor.

On the way to decarbonization, it cannot be missed that a new gas turbine is not enough to achieve combustion technology based on hydrogen, since challenges with extraction, collection and transportation of H_2 need to be considered and solved.

Presently, there is a global trend in researching and developing gas turbines fueled with hydrogen. Several different projects of developing hydrogen usage are conducted by academic and industrial areas. The main centers of research are DOE, Hitachi, Kawasaki, Siemens and GE. Countries like India, China, Australia and countries in Africa are not staying behind and they are developing hydrogen as an alternative to fossil fuels. All of those projects are briefly described in a recent paper by Maria du Toit et al. [4]. The authors in the mentioned paper present main applications of hydrogen in the case of power generation with usage of gas turbine, they would like to notice that main task of H_2 is the addition to other fuels or syngas combustion. In the presented cases the hydrogen content was not greater than 40 % of volume. Countries which are competing with each other on investigation and design of hydrogen gas turbines provide rapid development in the hydrogen economy field.

There is the existing possibility of burning pure hydrogen in large size, heavy-duty gas turbine like those worldwide known powered by natural gas. In 2017 an article [13] about gas turbine burner operating with a pure hydrogen as a fuel was released. Research was based on a lean premixed burner which was adapted from heavy-duty gas turbine burner, this change could be possible by implementation of new axial swirler and a co-flow injection system. All of the studies took place with the usage of a burner prototype at the test rig with atmospheric parameters. In the mentioned article all of the researchers took place in Italy and the prototype for the combustor was TG50 DLN. Specific hydrogen combustion characteristic forces out to rebuild the combustor of the gas turbine. Thanks to constant control of two factors, which were flow speed and premixing level, handling the flame inside burner was possible. Parameters such as equivalence ratio, thermal input and premixer unload rate were constantly changed over the extensive variety of values during research work. In the meantime, three challenges of using pure hydrogen as a fuel were monitored and noted, those problems are the following: flash-back limit, burner pressure drop and nitrogen oxides level of emission. After collection and analysis of the data, the authors conclude that more rapid velocity flow could be helpful in avoiding flame positioning during hydrogen burning inside the premixer duct. While outlet velocity would reach 130 m/s the level of emission of nitrogen oxides can be lower than 17 ppm. The numerical calculation of the system allows for comprehension of the dependencies between early ignition of the fuel and the operability of the burner.

Another hydrogen application as a fuel, reaching 100% content, in the commercial gas turbine has been reported by Cocchi and Sigali [14]. In this example the following project was developed by ENEL and GE Oil & Gas (ENEL - Italian multinational energy company, GE Oil & Gas division of General Electric – American multinational conglomerate). The tested gas turbine is GE10-1 model with a combustion chamber of a silo-type single can with diffusive flame combustor and rated power of 11.2 MWe. The project consisted of two stages, in the first zone 100% hydrogen fuel and limit of 200 ppmvd NO_x was assumed, either with or without steam injection, and in the second stage an improved combustor was assumed to emit less than 100 ppmvd of nitrogen oxide. After extensive research in the universities and factories the modified burner was created and tested on a full-scale at ENEL headquarters. Many parameters, for example metal temperature and pressure variation, were noted and compared to the prototype combustor unit. The first phase of the executed project allowed better understanding of the working CFD models and deduce improved design of burners. In the second phase, on the one hand it was important to achieve a configuration of the unit which will limit nitrogen oxide emission but on the other hand to ensure safe operation during burning of pure hydrogen. The authors of this paper noticed that in the design of the burner had very low impact on nitrogen oxide emission, metal and outlet combustor temperature. Opposite results were observed regarding flame instability, which is highly dependent of the burner design. Changes of NO_x level is dependent on liner design. The key feature in this reduction is air fuel ratio, but also penetration of air jets, which allow blending fresh air with exhaust products. On the other hand, higher air fuel ratio lower amount of cooling air, and this also results in growth of metal temperature. The limits of nitrogen oxide emission were kept by application of steam injection.

Both of the tested turbines mentioned above are working with air, that is why an important challenge to overcome is dealing with level of nitrogen oxides and carbon monoxides. For all the reasons mentioned earlier, stable development of hydrogen fueled gas turbine is visible but needs to be fully understood and the emerging technology needs to be better known and developed. With the purpose of reduction of the number of laboratory combustions tests, scientists nowadays are using calculation programs in order to simulate the behavior inside the combustion chamber and they are basing on numerical procedures for better reliability of the unit. Carbon-free power generation from burning hydrogen could be achieved in the near future, but it still requires research work.

3.5 MILD-OXY combustion of hydrogen

Concept of MILD (Moderate or Intense Low Oxygen Dilution) is combustion technique well-known for many years. This process was reviewed by Cavaliere and de Joannon [15] as a type of combustion where the temperature of the reactants at the inlet is higher than their auto-ignition temperature, while maximal permissible temperature rise corresponding to the inlet temperature is lower than the auto-ignition temperature. High temperature burned gases are recirculating with high velocities inside the combustion chamber. This technology is encouraging because the amount of pollutants, such as nitrogen oxides, can be reduced. The reason of this is more uniform distribution of the temperature inside the combustor in comparison to typical combustion processes, ignition appears at low-oxygen concentration environment. Another advantage of this technology is increased efficiency of the whole installation. The major advantage of MILD combustion is capability of burning various fuel types. MILD technology shares similar combustion characteristic with HiTAC (High Preheated Air Combustion), FLOX (Flameless Oxidation) or CDC (Colorless Distributed Combustion). All of those technologies depend on dilution of the fuel and air inside combustion chamber without occurrence of flame typical for combustion processes, which means narrow flame front.

For many years it was thought that in order to obtain MILD combustion properties the preheating of combustion air to temperature higher than ignition level is needed. In order to obtain increased temperature, regenerators were usually applied for recuperation heat from the flue gases. In nowadays solutions the oxidizer is injected into combustion chamber with velocity high enough to obtain recirculation inside for self-preheating of air and self-diluting of oxygen.

In the scientific literature many papers about MILD combustion can be found, but they are presenting analyses of combustors operating with usage of wide variety of fuels, this technology can be easily applied for low calorific fuels and high calorific industrial waste but there is still lack of knowledge in the topic of using hydrogen as fuel. This is due to the fact that combustion of hydrogen is very unstable but applying MILD combustion in this topic is very promising solution. MILD combustion technology not only solves the problems with combustor cooling, caused by high temperature of hydrogen flame, but also deals with unreacted hydrogen and oxygen in the outlet steam due to the fact of close to equilibrium composition state at the outlet.

OXY combustion is worldwide known technology adapted in order to capture carbon dioxide from exhaust fumes in coal combustion. It is based on substitution of combustion air by an oxidizer, which means application of pure oxygen and recycled flue gases. The drawback, in units where oxy combustion is applied, is the high cost of oxygen separation from air. On the other hand, the oxy combustion of hydrogen was applied in rocket engines and steam generators, but this technique is still not well described in the topic of power generation production.

In the context of rocket engine typically the gaseous hydrogen is combusted in the presence of the liquid oxygen. This technology meets couple issues like micro-scale transport, thermochemical phenomena and flame stabilization. In the context of burning hydrogen in rocket engines the combustion conditions are different from typical due to the use of liquid oxygen and very high flow velocities.

Oxy combustion of hydrogen takes place also in steam generators as a method of high temperature steam generation. This solution could be applied in conventional steam cycles as spinning reserve of additional steam, which was created from chemical reactions of hydrogen with oxygen. The design of steam generator consist of part of propellant injection, than combustion chamber which is cooled regeneratively and part where water is injected in order to cool down gases to the desired temperature, the last stage of steam generator is vaporization zone, where mixing and vaporization of injected water takes place - [16]. The conception of hydrogen/oxygen steam generators is struggling with main problem of large content of H_2 and O_2 in the combustion products, steam. Those residuals are unreacted reactant, which are impossible to avoid, because from [16] it can be concluded that increased temperature results in increased equilibrium concentration of hydrogen, but increased pressure makes the concentration decreased. This issue is getting worse in the case of low-pressure turbine.

The idea of combining MILD and oxy combustion technique was already implemented in the field of burning coal and it resulted with improved efficiency and limited emission on nitrogen oxides and coal oxide. Couple of different geometries of furnace were proposed, but the concept of hydrogen in those studies were skipped. Combination of those two techniques is very promising solution, in the future it could be applied in advanced steam cycle.

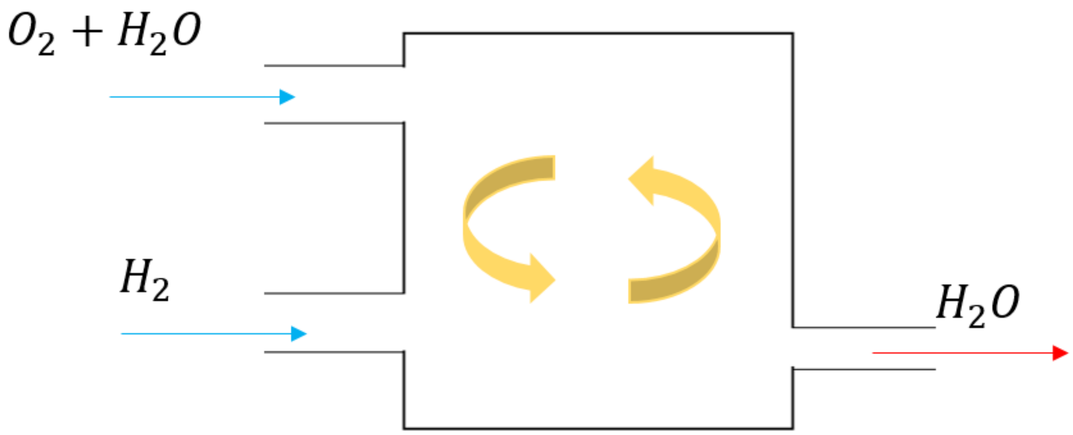

Figure 5 Concept of hydrogen combustion in diluted oxygen stream

3.6 Hydrogen based combustion cycles

The scientists analyzed and developed advanced steam turbine cycles in which the pure hydrogen can be burned in the presence of oxygen. Milewski reviewed in his paper [2] a couple of already developed concepts, where the common factor is the lack of external burning of fuel and presence of the boiler, instead of this the steam is generated in the combustion chamber where pure hydrogen is directly introduced. This idea brings behind clean usage of hydrogen, so called zero-emission, because in the combustion cycle the product in the process of electricity production is water. The concepts of the cycles presented in the paper [2] are based on the Rankine cycle and achieved efficiencies can be as high as in coal power cycles. The topic of main concern are high pressure 25 MPa and temperature reaches 1700°C, which could work whenever the limits of material for construction will be meet.

Milewski proposed, after analysis of other cycles, in the paper [2] his own concept of the cycle called Modified New Rankine Cycle (MNRC). Schematic cycle presented on figure 6 consists of three combustion chambers (CC) and three turbines (HPT, MPT, LPT – high, medium and low-pressure turbines), in front of every turbine there is a combustor which is operating at different pressures and H_2O flow rates. Strait after last turbine there is a heat recovery steam generator (HRSG) in the zone of low-pressure, from which steam is recycled back into the first combustion chamber. The combustion chambers where hydrogen content at the outlet is low enough to avoid appearance of explosive mixture of hydrogen and oxygen, still needs to be studied and developed. The methods used in rocket engines and steam generators could be used and adjusted in the hydrogen combustion cycle techniques.

The advantages of the cycle obtained from computationally predicted results are the very high efficiencies 77% (LHV based), low investment cost, high durability and power density, quick start-up. The discussed cycle, due to all qualities, besides the efficiency is far ahead from fuel cells.

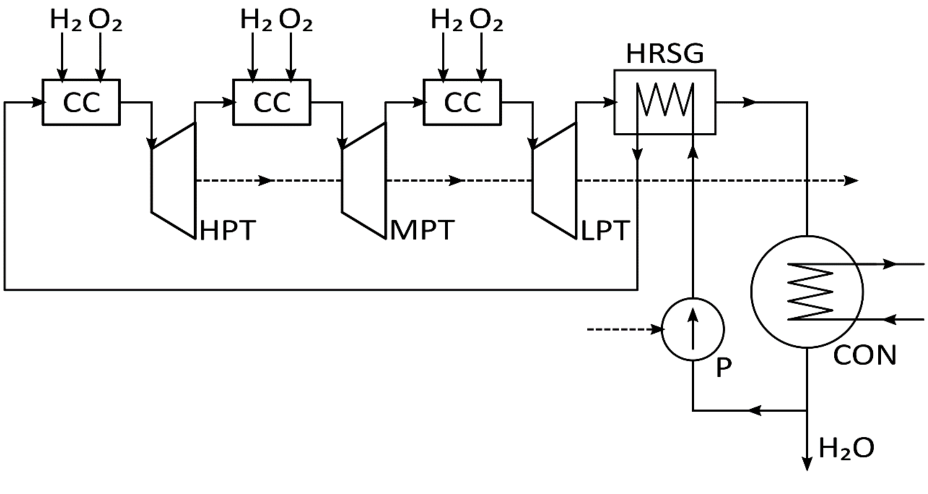

Figure 6 The MNRC cycle (based on [2]), where CON - condenser, P – pump.

4 COMPUTATIONAL MODEL

This chapter provides an overview of modelling aspects of the studies performed in this thesis. First of all, the reaction mechanism will be presented. Moreover, the computational methods carried out with the usage of Cantera software will be described. Cantera is a computational, open-source software with a package of tools created in order to solve problems of chemical kinetic, thermodynamic and transport processes. The users can resolve complex tasks such as multiphase chemical equilibrium, thermodynamic and transport properties, kinetics, time-dependent reactor network, one-dimensional and diffusion flames, reaction path diagrams. Cantera allows to be used by many different interfaces like C++, MATLAB, FORTRAN 90 and Python.

For the purpose of this master thesis Python was chosen as the most suitable option due to extensive and detailed online support, excellently prepared documentation, free and easily available usage. Plotting was performed by Matplotlib, data were analyzed with NumPy and reaction path diagrams were created with Graph viz. All those processes were conducted with usage of Anaconda distribution, which is manager of data science packages.

4.1 Reaction mechanism

In order to start computations with Cantera software the kinetic mechanism needs to be selected for the fuel which will be subject of the studies. The set of data available for Cantera software include many different types of mechanisms and each of them counts multiple species and reactions. For the purpose of this thesis the h2o2 mechanism was selected, which is also a subset of very well-known GRI-Mech 3.0 mechanism, most popular chemical scheme. Every user has also possibility of writing down a mechanism in specified Cantera software. Hydrogen-Oxygen (h2o2) mechanism contains 3 elements, 9 species and 28 reactions [3].

4.1.1 Hydrogen oxidation

The mechanism of description of combustion of hydrogen has been tested and is well established to gather information about burning velocity, ignition delay time, temperatures. The initialization of a chemical chain system starts mainly by the following reaction [19]:

$$H_2 + O_2 \rightleftharpoons H + HO_2$$

After the main initiation reaction, the oxidation of hydrogen takes place and the chain-branching system begins. The high temperature conditions are the reason why the combustion occurs in the explosive regime (580 °C). [19]

$$H + O_2 \rightleftharpoons O + OH$$

$$H_2 + O \rightleftharpoons H + OH$$

$$H_2O + O \rightleftharpoons 2OH$$

$$H_2 + OH \rightleftharpoons H + H_2O$$

If only the temperature is lower or the pressure becomes higher the reaction of creation of HO_2 radicals plays an important role, because of the collision third-body reactant M which happens to have different efficiencies of energy transfer of activated complex [19].

$$H + O_2 + M \rightleftharpoons HO_2 + M$$

The following reactions decrease the rate of fuel-oxidation and they are expanding chain of reactions [19]:

$$HO_2 + H \rightleftharpoons OH + OH$$

$$HO_2 + OH \rightleftharpoons H_2O + O_2$$

$$HO_2 + HO_2 \rightleftharpoons H_2O_2 + O_2$$

The process of rapid oxidation in a flame is followed by high temperature and presence of H and O radicals, which are reacting in the postflame section which is coupled with release of heat and maintenance of H and O radicals at equilibrium level. Those reactions are characterized as three-body and the main is [19]:

$$H + OH + M \rightleftharpoons H_2O + M$$

4.1.2 Chemical kinetics

Chemical kinetics is the study which handles rate of chemical reactions, where molecules, two or more, are interacting with each other by collision and they are transforming from reactants into products. This formation of new species, after break of bonds is called rate law or reaction rate. An overall chemical reaction is given by an equation [20]:

$$A + B + C + \cdots \overset{k_{f,b}}{\Longleftrightarrow} D + E + F + \cdots, \tag{1}$$

where reactants are $A, B, \ldots$ and products of reaction are $D, E, \ldots$. The reaction rate when consumption of reactant A is taken into consideration can be formulated as [20]:

$$\frac{d[A]}{dt} = -k_f \cdot [A]^a [B]^b [C]^c \ldots \tag{2}$$

In the formula above the $a, b, \ldots$ are the reaction orders in relation to $A, B, \ldots$ species, $[\mathrm{A}]$, $[\mathrm{B}]$, ...are the mole concentration (kmol/m^3) and k is the rate coefficient of the reaction. The reaction is reversible, and the reaction rate of the backward reaction takes the following form [20]:

$$\frac{d[A]}{dt} = k_b \cdot [D]^d [E]^e [F]^f \ldots \tag{3}$$

When the reaction is at chemical equilibrium on the microscopic level the forward and backward reaction have the same rate, but when it comes to macroscopic level the net reaction rate is equal to zero. The equilibrium constant Kc can be defined as [20]:

$$K_c = \frac{k_f}{k_b} = \frac{[A]^a [B]^b [C]^c \ldots}{[D]^d [E]^e [F]^f \ldots} \tag{4}$$

An elementary reaction is happening on the molecular level exactly as it is described by the reaction equation. The orders of reaction as $a, b, c\ldots$ dependent on time and reaction conditions and they follow molecularity of the elementary reaction. The reaction mechanism is a set of elementary reactions. Three types of molecularity of reaction are defined: unimolecular (first order rate law), bimolecular (second order rate law) and trimolecular (third order rate law). Mentioned types of reactions can be presented as follows [20]:

$$A \rightarrow products$$

$$A + B\ (or\ A + A) \rightarrow products$$

$$A + B + C\ (or\ A + A + B\ or\ A + A + A) \rightarrow products$$

As can be observed to the order of elementary reaction is equal their molecularity. The equation of an elementary reaction r is as follows [20]:

$$\sum_{s=1}^{S} v_{rs}^{(e)} A_s \overset{k_r}{\rightarrow} \sum_{s=1}^{S} v_{rs}^{(p)} A_s, \tag{5}$$

where A_s is the chemical formula of species A_s, and $\mathrm{v}_{\mathrm{rs}}^{(\mathrm{p})}, \mathrm{v}_{\mathrm{rs}}^{(\mathrm{e})}$ are the stochiometric coefficients of the reactant $s=1,\ldots,S$, (p) and (e) presents the product and reactant species, and k is the forward reaction rate of reaction r.

Then the rate law of the species *i* formation in one particular reaction is the following [20]:

$$(\frac{\partial c_i}{\partial t})_{chem,r} = k_r(v_{ri}^{(p)} - v_{ri}^{(e)}) \prod_{s=1}^{S} c_s^{v_{rs}^{(e)}} \tag{6}$$

where c_i is the concentration of species *i=1,...,S,* and c_s is the concentration of all reactant species in the reaction *r* other than *i.*

The summation over the rate equations of all elementary reactions *r=1,...,R* gives the total rate of formation/destruction of a species *i*. [20]

$$\dot{\omega_i} = (\frac{\partial c_i}{\partial t})_{chem} = \sum_{r=1}^{R} k_r\,(v_{ri}^{(p)} - v_{ri}^{(e)}) \prod_{s=1}^{S} c_s^{v_{rs}^{(e)}} \tag{7}$$

The rate coefficients are in most cases highly dependent on temperature and this relationship is nonlinear. The law presenting this dependence is called the Arrenhius law, and a modified three-parameter form is given by [19]:

$$k_f(T) = AT^{\beta}e^{\frac{-E_a}{RT}}, \tag{8}$$

by the addition of the T^{β} term equation (8) differs from the usual Arrenhius law form. β is a temperature T modifier exponent, and A is a pre-exponential factor, E_a is the activation energy, needed for initialization of the reaction and R is the universal gas constant. The Arrenhius law is important in terms of the chemical kinetic reaction mechanism [3], where all mechanism is made up of the mentioned above parameters.

4.1.3 Thermodynamic properties

Cantera software is using the NASA 7-coefficient polynomial parameterization to provide data about thermodynamic state of the species, such as specific heat c_p, enthalpy h and entropy s. Every species of the phase can implement various parameterization for characterization of the dependence of the heat capacity on the temperature. The thermodynamic quantities can be reproduced by the following equation [21]:

$$\frac{c_p(T)}{R} = a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4 \tag{9}$$

$$\frac{h(T)}{RT} = a_0 + \frac{a_1}{2}T + \frac{a_2}{3}T^2 + \frac{a_3}{4}T^3 + \frac{a_4}{5}T^4 + \frac{a_5}{T} \tag{10}$$

$$\frac{s(T)}{R} = a_0lnT + a_1T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + a_6 \tag{11}$$

here coefficient from a_0 to a_6 can be given for one or a few temperature ranges.

4.2 Reactor theory

The choice of simulation fell on the ideal gas reactor, to be exact Well-Stirred Reactor (WSR), also denoted as continuously Stirred Tank Reactor (CSTR), Perfectly Stirred Reactor (PSR). This reactor was used to study chemical kinetics of hydrogen combustor and basically this is a single Cantera reactor with inlet, outlet and fixed volume [3]. On the figure below the scheme of the discussed reactor is presented, the combustible gases with mass-flow rate $\dot{m}$, a temperature T^* and mass-fraction composition Y_k^* enter the reactor. In this type of modelling it is assumed that entering gases are mixed perfectly and continuously with gases already present inside the reactor. As a result, temperature and composition are uniform.

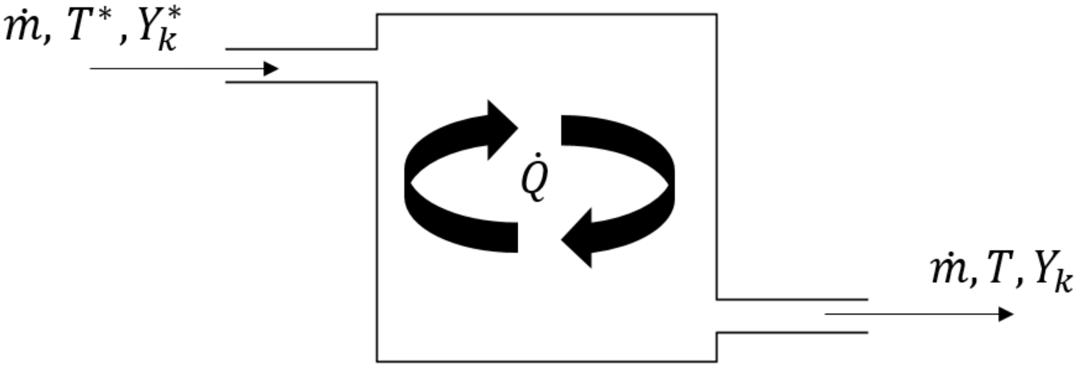

Figure 7 Schematic diagram of well-stirred reactor based on [19].

Chemical reactions inside the well-stirred reactor are occurring homogeneously inside all volume of the reactor and they are depending on temperature inside the reactor, composition of reactants and residence time. In the steady flow it is assumed that mass flow on the inlet and the outlet is unchanged. The temperature and mass fraction composition are the same inside the reactor and at the outlet.

In the real life cases the stirring cannot be instantaneous, that is why the well-stirred reactors are intended to cause turbulence of high intensity which improves mixing. The reactors operating with low pressure can also be assumed to work as stirred-reactors, due to the fact that in low-pressure system the molecular-diffusion rate is very-high due to long paths. The described way of mixing results in maintaining the temperature and composition homogeneous inside the reactor.

The governing equations for a well-stirred reactor with adiabatic walls (without consideration of surface reactions at the wall) are presented below.

Mass Conservation [19]

$$\frac{dm}{dt} = \sum_{in} \dot{m}_{in} - \sum_{out} \dot{m}_{out} \tag{12}$$

where m is the mass of reactor's contents, t is time, $\frac{dm}{dt}$ is the change in mass in well stirred reactor as the result of flow through inlets and outlets of the reactor, $\dot{m}_{in}$ is the mass flow rate at the inlets and $\dot{m}_{out}$ is the mass flow rate at the outlets.

Species conservation [19]

$$\frac{dY_k}{dt} = \sum_{in} \frac{\dot{m}_{in}}{\rho V}\left(Y_{k,in} - Y_k\right) + \frac{\dot{\omega}_k W_k}{\rho} \tag{13}$$

where Y_k is the mass fraction of species k in the well-stirred reactor, given by $Y_k = \frac{m_k}{m}$ where $m_k$is the mass of species k. $Y_{k,in}$ is the mass fraction of each species k at the inlets, V is the reactor volume, $\dot{\omega}_k$ is the molar production rate of species k and ρ is the density of mixture inside the reactor given by the ideal gas equation of state [19]:

$$\rho = \frac{p}{(RT \sum_k \frac{Y_k}{W_k})} \tag{14}$$

where p is the pressure, R is ideal gas constant, T is temperature, and W_k is the molecular weight of species k.

Energy conservation [19]

$$c_p \frac{dT}{dt} = -\sum_k \frac{h_k \dot{\omega}_k W_k}{\rho} + \sum_{in} \frac{\dot{m}_{in}}{\rho V}\left(h_{in} - \sum_k h_k\, Y_{k,in}\right) \tag{15}$$

where c_p is the specific heat capacity, h_k is the specific enthalpy for species k and h_{in} is the specific enthalpy of the inlet composition.

In the steady state cases, the mass flow rate is unchanged and equal at the inlet and outlet and the time derivative in the governing equations is equal zero. The result of this is that the set of ordinary differential equations reduces to a set of coupled nonlinear algebraic equations. In order to solve the set of those equations the Newton solver could be implemented, but because of occurrence of nonlinearities and possibility of multiple solutions a more advanced way of solving the problem needs to be considered. Unfortunately, the Cantera software does not use the Newton solver and the steady-state well-stirred reactor simulation are solved with volume and time-dependent reactor with determined inlet and outlet properties. The equations, with some initial condition are advanced in time till the moment of converged state of solution.

5 RESULTS AND DISCUSSION

In this chapter, the results obtained from calculation with Cantera are presented. The number of simulations of kinetics of hydrogen combustion were carried out. The task involved getting acquainted with programming language, preparation of scripts in Python software and computations which were time consuming, due to amount of calculated cases.

The computations performed using Cantera involved:

- Equilibrium computations – here the ‘Equilibrate’ solver was used to obtain equilibrium composition, temperature and pressure at various initial set conditions.
- Reactor modelling – here an ‘IdealGasReactor’ model was used to predict the evolution of species and temperature in time for an initial set of conditions.

To briefly describe the set of 4 basic steps needed to be performed in order to work with Cantera and run program to simulate reactor reactions. In first step in Python software the module called Cantera needs to be imported. Next from the library of many different mechanism, the one that has chemical scheme corresponding to studied fuel needs to be chosen and the set of initial conditions for this gas should be defined. They are many different properties which can be defined to set the state of gas, mainly temperature, entropy, enthalpy, density, pressure and mole or mass fractions. In the following step the type of reactor containing the gas state should be selected and defined. With all that information in last step the simulation can be carried out from which states of the gas are obtained with all changes which are advancing in time. The output from the performed simulation can be presented as the numerical set of data but in order of better presentation of obtained solution it can be shown as a plot.

The reaction path diagram is obtained after application of the reaction path analysis and this graphical way of presentation of the solution describes the net element flux (measured in units kmol/m^3/s) among species at some point in time in the evolution of the chemistry. Figures 8 and 9 present the reaction path diagrams of hydrogen on the way of fuel burning in the reactor. The gases introduced into the reactor were at stoichiometric values of H_2, O_2 and H_2O, which represents oxy combustion of hydrogen with steam dilution. Those path diagrams help in better understanding reaction including hydrogen in the simulation of burning. Those two diagrams were generated at 750 K temperature at the inlet of the reactor. Figure 8 presents the simulation conducted at pressure 1 bar which is low-pressure case and figure 9 presents a case with much higher pressure which is 250 bar understood as high-pressure example. Based on those two cases we can observe that hydrogen oxidation kinetics is very different with the dependence of pressure. Large number of reaction paths on diagram helps in better understanding of kinetics mechanisms. The values appended to every arrow present the net element flux of hydrogen atom. The scale provided under the diagram is the scale of normalization of the values presented on the arrows against the maximum net element flux. The thickness of an arrow corresponds to the values of the net element flux.

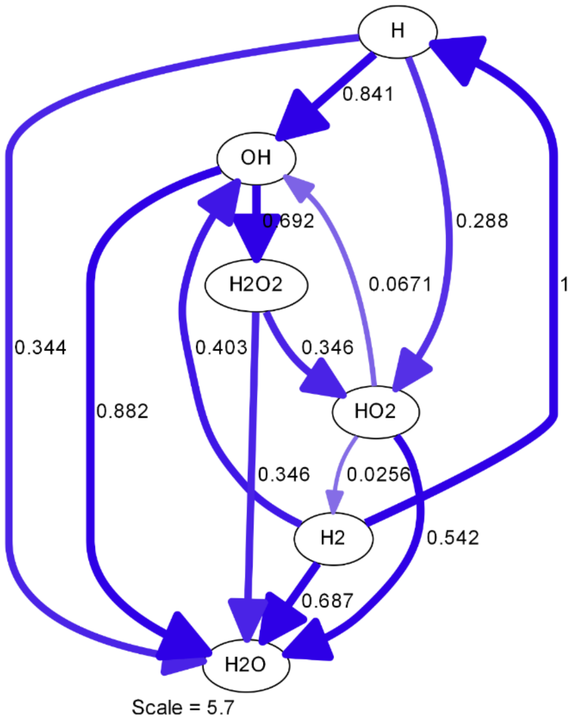

Figure 8 Reaction path diagram following hydrogen at temperature 750K and pressure 1 bar.

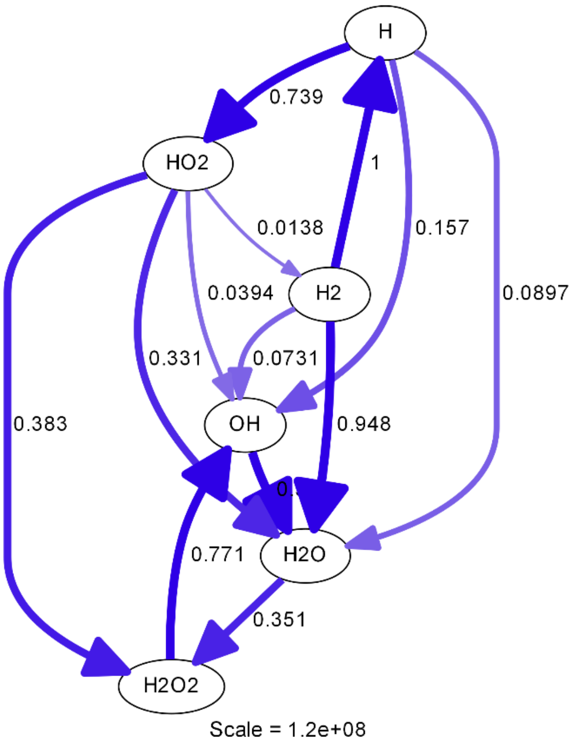

Figure 9 Reaction path diagram following hydrogen at temperature 750K and pressure 250 bar.

5.1 Gas equilibrium

Chemical equilibrium is the state when in a chemical reaction the concentration of products and reactants do not vary in time. The chemical equilibrium can be also described by the rate of reaction it means that forward and reverse reactions share this same rate, which in overall is not zero but it is equal each other. This equality of rate results in lack of net changes in the concentration of reactants and the products it is so called dynamic equilibrium with a constant described as equilibrium constant. The chapter 4.1.2 presents wider knowledge about equilibrium and the equation which rules rate constants. A change of temperature or concentration of reactants and products can influence the equilibrium state. A change of pressure can also influence the equilibrium state but only when the number of gas molecules in the products and reactants differ, but on the other hand when those numbers of gas molecules is the same, then pressure will not have influence on state of equilibrium anymore.

The equilibrium constant is associated with the standard Gibbs free energy change of the system. Chemical equilibrium state at constant pressure and temperature is achieved when the Gibbs energy is minimized.

In order to define gas equilibrium, the program in Python software was written which comes with the Cantera source file. From the Cantera library 'h2o2.xml' mechanism was imported and adapted as a gas object in simulation.

The aim of the equilibrium computations was to determine the composition of H_2-O_2-H_2O system at various conditions. Such computations are useful to predict how much unreacted O_2 and H_2 will be present at the outlet of a combustor, if the residence time would be 'long enough', i.e. the real composition would be approaching the equilibrium composition. The equilibrium state is therefore treated here as a limiting state.

Initial properties of the gas introduced to the calculations are values of pressure and temperature:

- values of pressure: 1, 10, 50, 100, 150, 200, 250 bars
- values of temperature: from 1073 till 2500 K every 50 Kelvin degrees.

The initiated function used to find out the equilibrium state of the gas is called 'equilibrate' and in the case of this thesis the temperature and pressure ('TP') were used for computation. The equilibrium state is obtained by minimizing the Gibbs free energy holding temperature and pressure constant, i.e. the system is non-adiabatic. The initial temperature and pressure are therefore also the final temperature and pressure. Beside those two properties introduced at initialization of the gas, the mole fraction of the examined chemical species is also used in the function. In this case the mole fraction and type of the examined substance is 1 mole of H_2O. The input file, here 'h2o2.xml', and all species and reactions subscribed to this file are responsible for the chemical species and composition of the products.

The outcome of the simulation carried out is the set of properties like enthalpy, internal energy, entropy, Gibbs function and heat capacity at constant pressure and volume. Another result of the simulations is the mole fraction of species at equilibrium state, calculated at given temperature and pressure. The set of data include species like diatomic gases of hydrogen (H_2) and oxygen (O_2), water (H_2O), hydroperoxyl (HO_2), hydrogen peroxide (H_2O_2) and ions of hydrogen ($H+$), oxygen (O_2-), hydroxide ($OH-$). The equilibrium states of main of those species are presented on figure from 10 to 15. The plots presented on those figures were created by one of the packages of Python software, namely Matplotlib. On the plots in this subsection all of the introduced mole fractions are presented in logarithmic scale which allows easier reading and better presentation of the results.

The composition of the reactants at equilibrium state presents the outcome after the infinite time of reaction. The equilibrium state is stable and complete result of the simulation and a Cantera code determines the solution independently of residence time, that means that residence time in equilibrium calculations needs to be long enough for all species have been reacted.

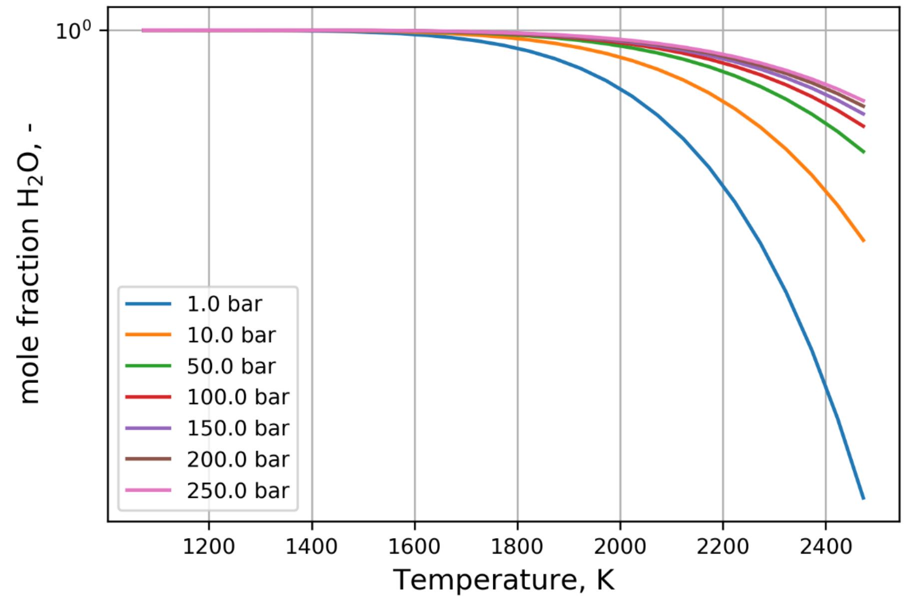

Figure 10 Mole fraction of H2O at specific temperature and pressure of gas in equilibrium.

The mole fraction of steam, presented on figure 10, is decreasing because independently of the type of molecule. They undergo the dissociation, in this case the rise of temperature of steam is increasing this same happens with the amount of internal energy which is used in dissociation of water molecules. In the equilibrium state the partial dissociation could be observed at infinite time.

The rapid decrease of water molecules starts at around 1600 K and the case characterized by the biggest intensity of dissociation is the case of low-pressure which means 1 bar. The tendency of changes of H2O mole fraction is downward with the growth of temperature. At the pressure equal to 250 bar the mole fraction of steam is the highest but with a drop of pressure the value of mole fraction is decreasing.

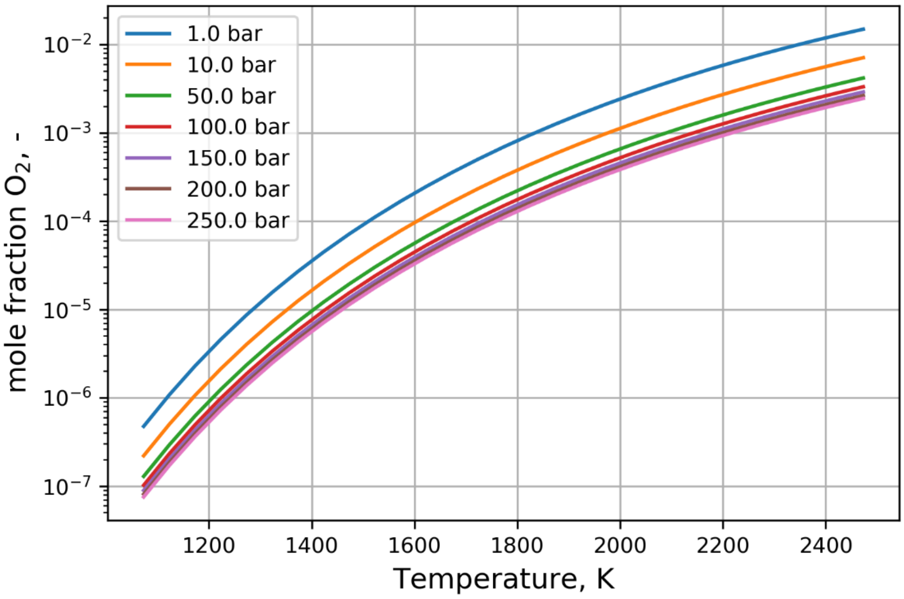

Figure 11 Mole fraction of O2 at specific temperature and pressure of gas in equilibrium.

The mole fractions of oxygen and hydrogen at defined temperature and pressure is presented on figure 11 and 12. In the result of equilibrium simulation those two molecules share the highest mole fraction after the steam mole fraction. The calculated values of O_2 and H_2 are of almost the same order, from 10^{-7} till 10^{-1}. Those cases share this same trend in the changes of molecular quantities, which is increase of values of mole fraction together with growth of temperature. On the other hand, the bigger values of pressure are associated with smaller H_2 and O_2 concentrations.

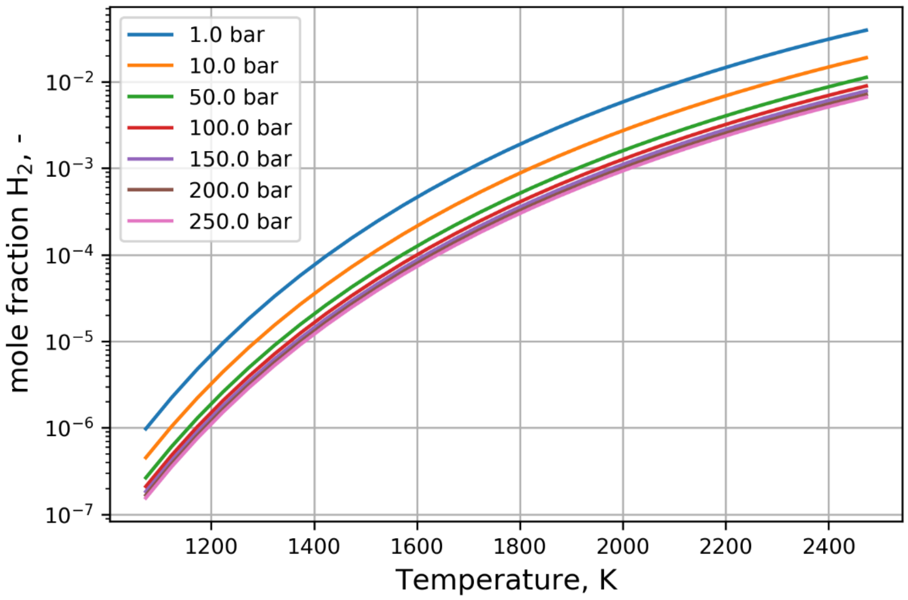

Figure 12 Mole fraction of H2 at specific temperature and pressure of gas in equilibrium.

The case of 1 bar, marked with blue line on the plots, is the low-pressure example in which the mole fractions are the biggest in all examples. When it comes to hydrogen the problem appears in low pressure turbines where the concentration of this combustible gas can be dangerous and harmful for components of a cycle behind the turbine. Whenever some leftovers of hydrogen and oxygen molecules will get through last turbine unreacted and their concentration will be higher than the lower flammability limit, the mixture can ignite and explode which will be destructive for the part of cycles. This phenomenon can be dangerous for the condenser in Figure 6, where after water vapor condensation the remaining gaseous H2 and O2 can accumulate and form combustible mixture. This hazardous phenomenon needs to be avoided.

A solution to that phenomenon can be a catalytic converter placed after the lowest turbine stage, facilitating conversion of the H2 and O2 to H2O. This however would result in higher cost and drop of efficiency due to energy losses and pressure drop.

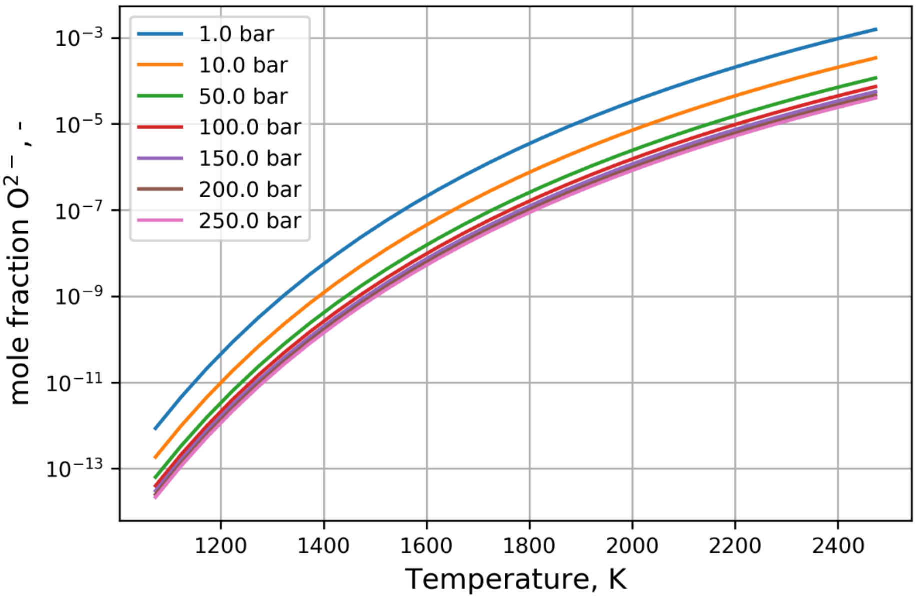

Figure 13 Mole fraction of O ions at specific temperature and pressure of gas in equilibrium.

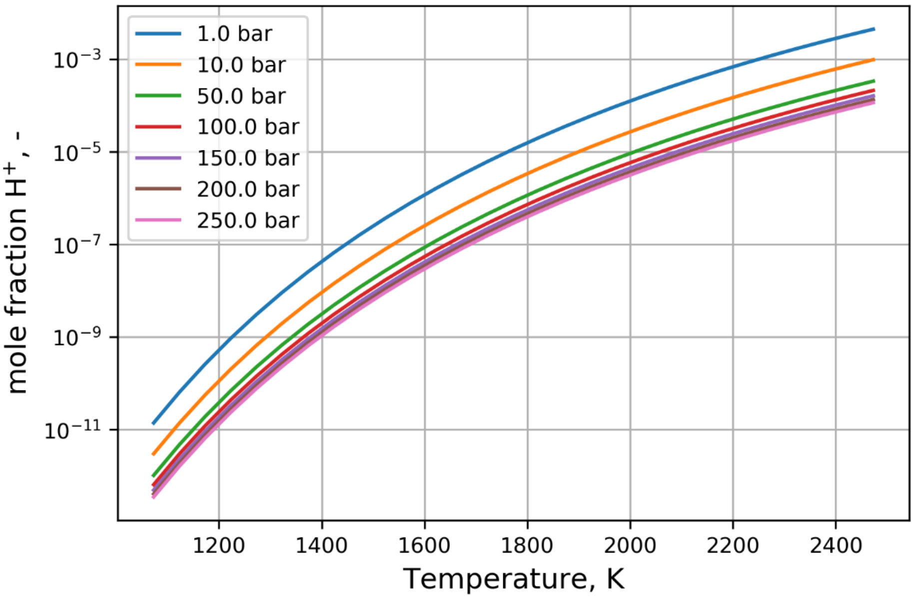

Figure 14 Mole fraction of H ions at specific temperature and pressure of gas in equilibrium.

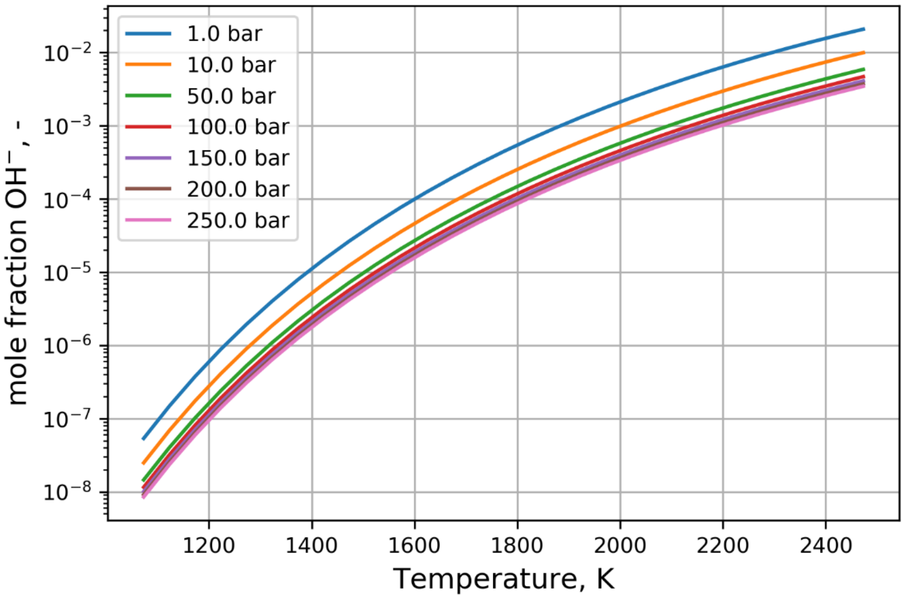

Figure 15 Mole fraction of OH ions at specific temperature and pressure of gas in equilibrium.

On the figure from 13 till 15 the trend of changes of mole concentration is analogous to this described on the basis of figure 11 and 12. The concertation of ions in this simulation is lower in comparison to previous mole fractions.

5.2 Reactor modelling

In order to mimic the oxycombustion of hydrogen in MILD like mode, the built in Cantera IdealGasReactor model was used. The kinetics of hydrogen combustion was calculated with the usage of open source Cantera software. A calculation program was prepared in which the build in reactor model allowed for determination of the volumes of the reactors and residence times of hydrogen combustion. The process of combustion will be achieved only when the searched volume and residence time will be large enough such that it will allow for ignition of the mixture. Moreover, increasing the volume and residence time in the reactor further, allows to determine such a volume and residence time, for which the combustion products composition is close to the equilibrium composition. This means that one can find the volumes of the reactors for various conditions at which the combustion is close to completeness. As presented in Fig.6, the three combustion chambers are operated at three different pressures, and slightly different steam inlet temperatures and flowrates. Therefore, the combustors will have different volumes and will be characterized by different residence times.

The simulation assumed searching of volume and residence time of the reactor on the assumption of power produced by the unit equal to 1 MW. This data allows for calculation of mass flow rate in the reactor, which was done with equation (16) presented below:

$$\dot{m} = \frac{P}{LHV} \tag{16}$$

where $\dot{m}$ is mass flow rate, P is produced power and LHV is Lower Heating Value.

The Lower Heating Value of gaseous fuel hydrogen is given as 120 MJ/kg based on [22]. The calculated mass flow rate was then substituted to equation for residence time of the reactor:

$$tr = \frac{V * \rho}{\dot{m}} \tag{17}$$

where tr is the residence time, V is the volume and ρ is the density of the gases inside the reactor. The density of gases was calculated in every case based on given temperature and pressure at the inlet. The calculations were performed with the set of data presented in Table 2:

Table 2 Thermodynamic properties.

Inlet Temperature, K	Inlet Pressure, bar(s)
300	1
500	100
700	250
800	

The given thermodynamic properties were implemented into calculations in every possible combination of inlet temperature and pressure. The cases of selected pressure represent three types of pressure turbines low-, medium- and high- pressure turbines (look at Fig. 6). The mechanism selected for calculation from the Cantera library was this same as previously ‘h2o2.xml’, because the set of reactions, possible phases and chemical species included is most suitable considering the topic of concern of this thesis. It should be stressed that many other H2-O2 reaction mechanisms exist, and new are continuously developed. The high pressures examined within the thesis are higher than those for which the used mechanism was developed. It was therefore assumed, due to lack of data, that this extrapolation is acceptable.

Better understanding of the concept of performed analysis and the layout of reactor with inlets and outlet is presented on Figure 5. The simulations performed in the thesis were based on stoichiometric process of burning hydrogen in oxygen diluted with water steam. The mass ratio of oxygen to hydrogen is $\frac{m_{O_2}}{m_{H_2}} = 8$, which is the effect of the chemical reaction given below:

$$2H_2 + O_2 \rightleftharpoons H_2O$$

One molecule of hydrogen H2 with molar mass 2 kg/kmol is reacting with one atomic oxygen O with molar mass 16 kg/kmol. In every simulation one mole of hydrogen was burned with 0.5 mole of oxygen, for those amounts the ratio of diluted water was proposed in three cases 1, 3 and 5 moles of H2O. Proposed properties and compositions were based on the analysis presented in MSc thesis of Wojtas [23] on hydrogen utilization in steam cycles, where the molar ratio of recirculated stream of H2O to the introduced stream of H2 was shown to be approximately 1:3.

The chemical energy of hydrogen is converted into thermal energy of the gaseous products. This process takes place in the reactor and for the purpose of this simulation the type of well-stirred reactor was chosen. In this type of reactor, the volume and residence time are important input data but in this thesis the problem of combustion hydrogen was reversed, and those data are sought in this simulation on the basis of the assumed chemical energy input.

In the solution described above there may appear a problem with the ignition of the well-stirred reactor, whenever the outcome of simulation is trivial and parameters at the inlet and outlet are identical it means that reactants are not reacting. The solution of this can be increasing the temperature or radical concentration at the initialization step.

5.2.1 Influence of reactor volume on combustion kinetics

The volume of the combustion chamber is dependent from set of various variables such as type of fuel injected, temperature and pressure of combustion. The calculations of combustion chamber volume were determined iteratively by the code developed within the thesis in Python, that uses the Canter code. In order to facilitate the computations, various set of possible volumes were introduced for different set of thermodynamic properties. The values of proposed volumes were decreasing.

Verification of the desired volume is important in determination whether the reactions are complete, i.e. close to equilibrium, or not. In the case where combustion chamber is too large, then compression ratio is lower which brings with it lower efficiency. Much bigger problem occurs when the volume is too small, then the amount of hydrogen at the outlet increases. The concentration of this gas at the outlet of combustion chamber needs to be as low as possible, due to the fact that hydrogen can create an explosive mixture with oxygen and the explosion could destroy the condenser.

In figure 16 till figure 27 the results from the simulation are presented. The obtained volumes of reactors are presented with logarithmic scale for clearer understanding. It can be observed on the following figures that with the increase of pressure and temperature at the inlet the volume of the reactor is decreasing. Although in the case of higher inlet temperature this variation of volume is not that visible.

Taking into consideration only one group of pressure, for example 1 bar, with various inlet temperatures, the volumes in which combustion process would be fulfilled are in the following range:

- Volume 10^{-7} m^3 – 10^{-6} m^3 with one mole of dilution steam
- Volume 10^{-7} m^3 – 10^{-5} m^3 with three mole of dilution steam
- Volume 10^{-6} m^3 – 10^{-3} m^3 with five mole of dilution steam

It means that volume of the reactor is strongly dependent on the pressure at the inlet of the reactor, taking into consideration those same compositions at the inlets of the combustion chamber

After the simulations it can be also observed that volumes of reactors at pressure 100 or 250 bars where 1 MW of power is produced, are very small, like 10^{-11} m^3.

Combustion of hydrogen diluted with one mole of H_2O, independently of inlet pressure and temperature, starts to react at the smallest volume. Therefore, increase of the amount of mole of H_2O in combusted mixture connects unambiguously with increase of the volume needed to start the reaction.

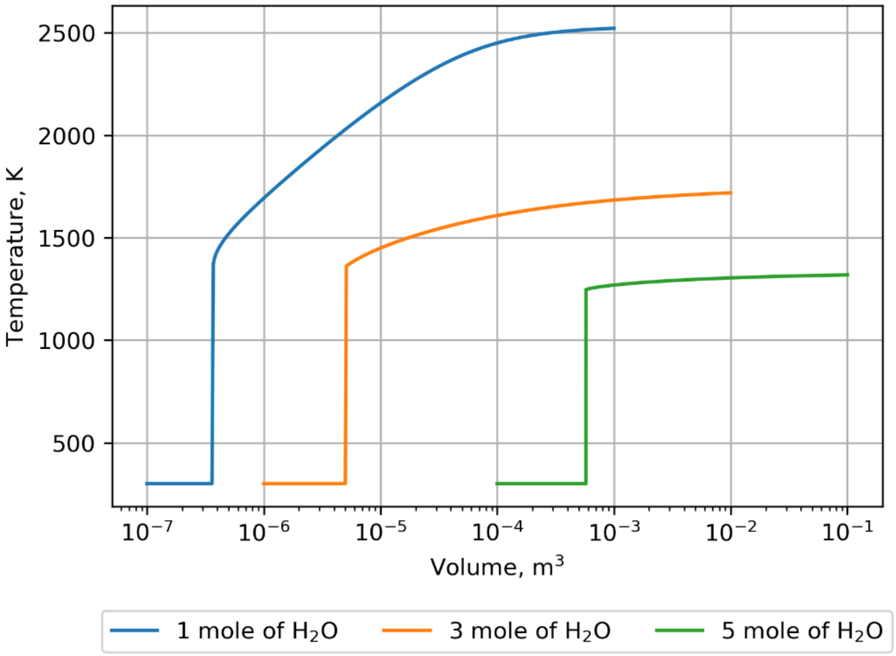

Figure 16 Volumes of the reactors at T_in=300 K and p_in=1 bar.

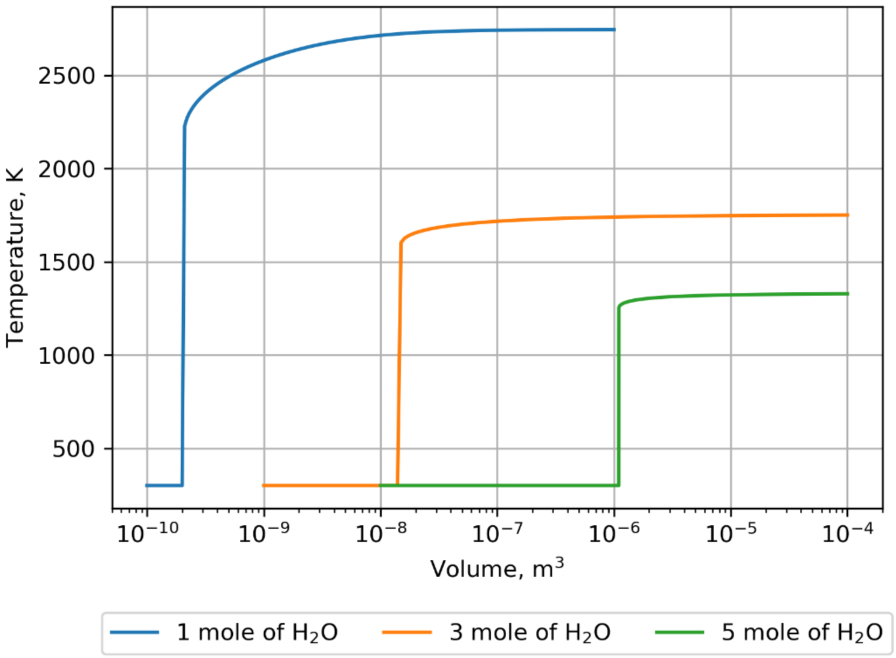

Figure 17 Volumes of the reactors at T_in=300 K and p_in=100 bar.

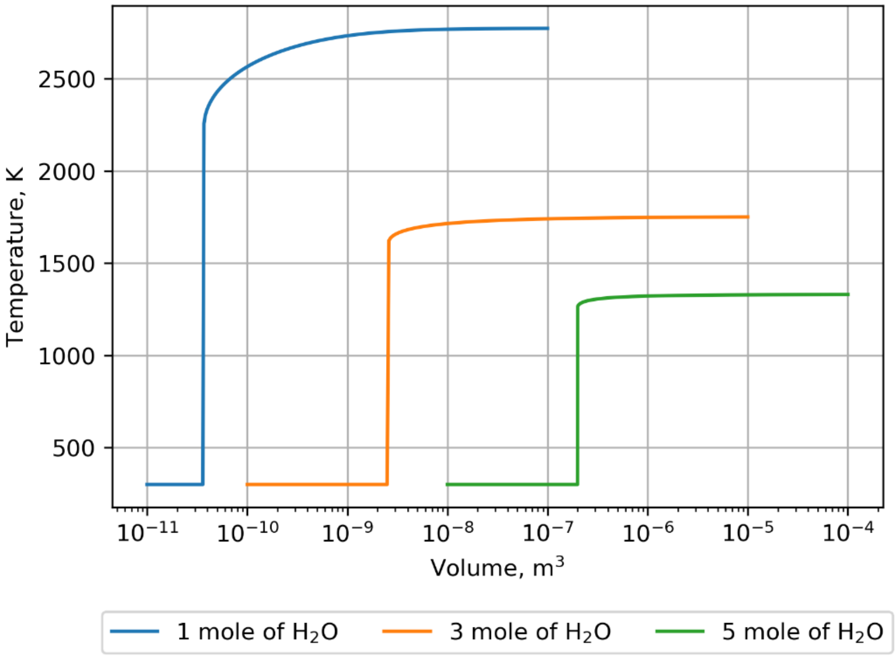

Figure 18 Volumes of the reactors at T_in=300 K and p_in=250 bar.

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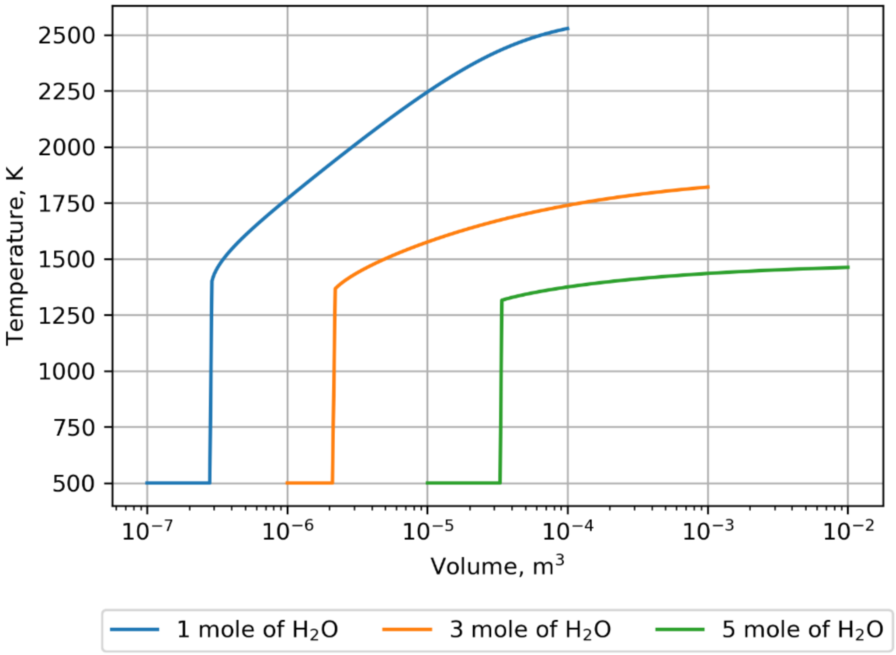

Figure 19 Volumes of the reactors at T_in=500 K and p_in=1 bar.

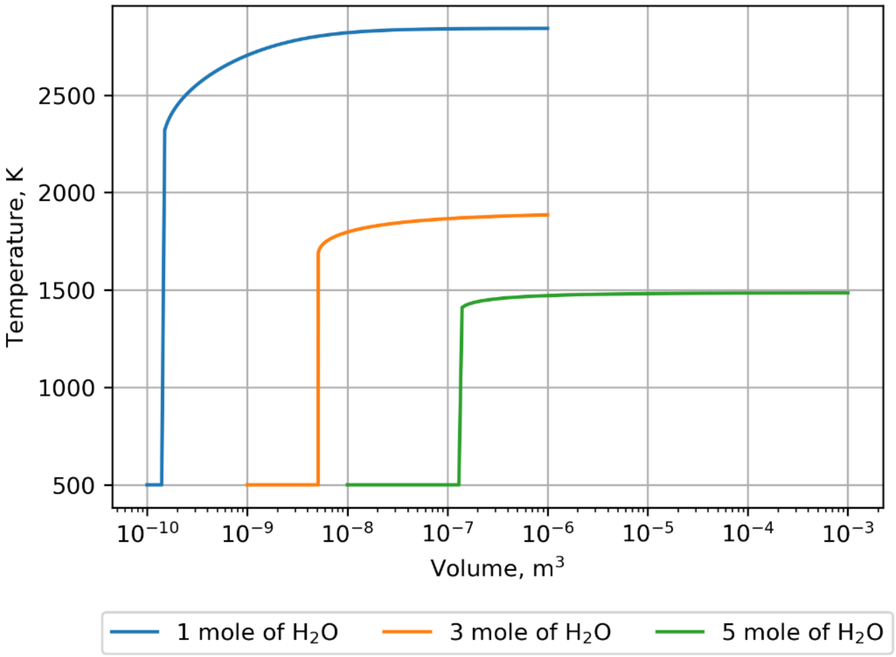

Figure 20 Volumes of the reactors at T_in=500 K and p_in=100 bar.

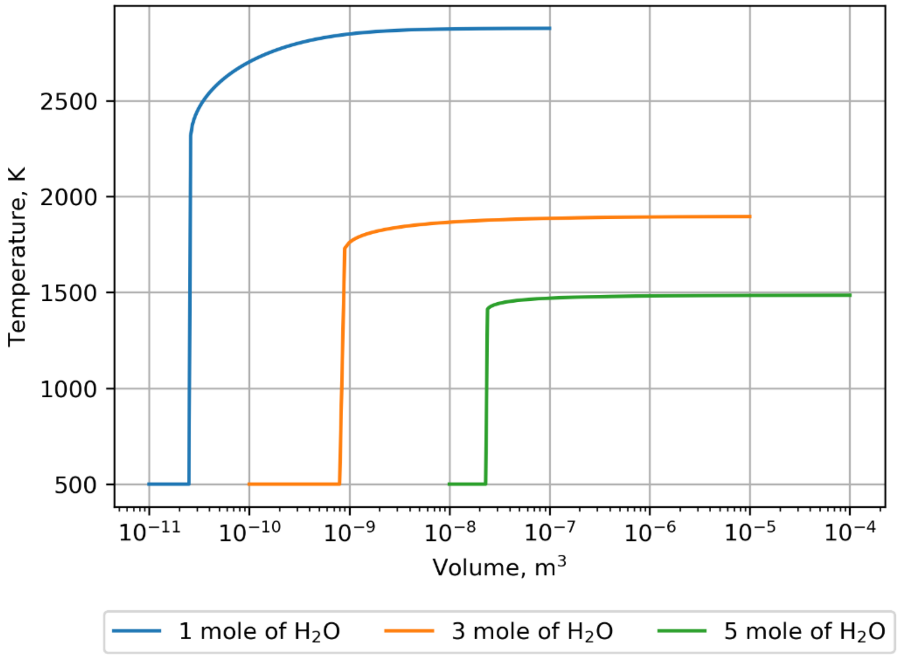

Figure 21 Volumes of the reactors at T_in=500 K and p_in=250 bar.

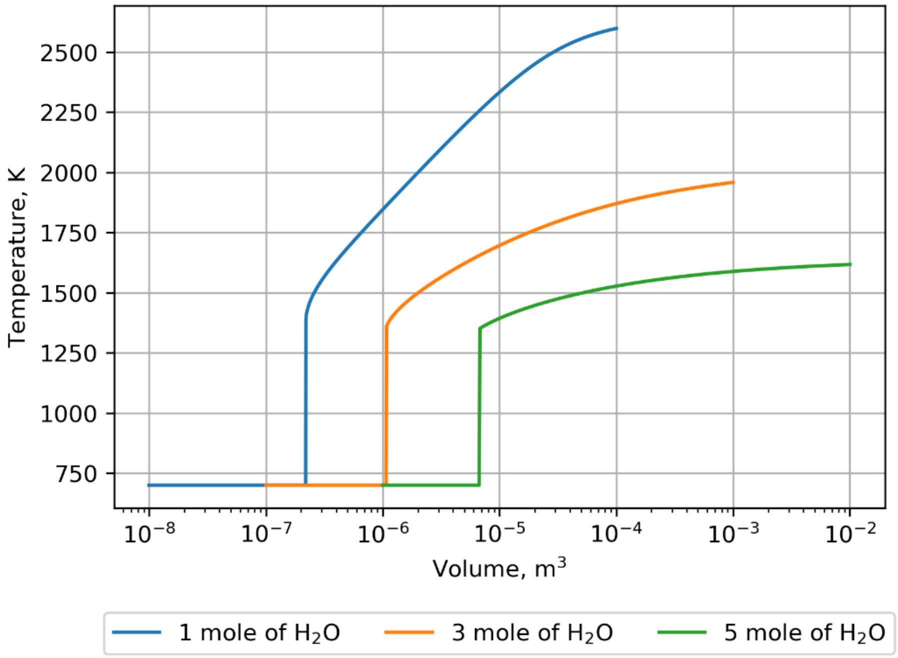

Figure 22 Volumes of the reactors at T_in=700 K and p_in=1 bar.

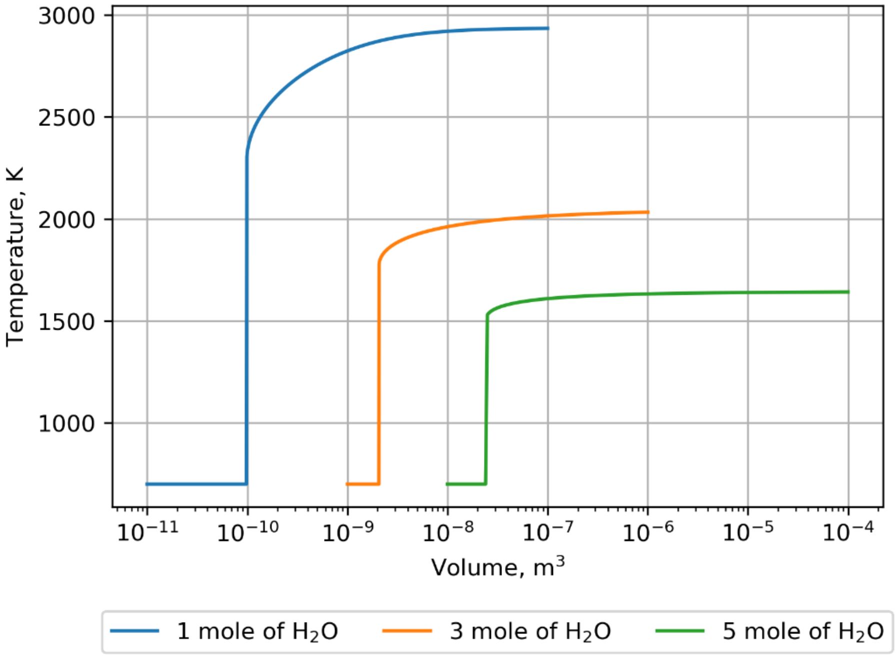

Figure 23 Volumes of the reactors at T_in=700 K and p_in=100 bar.

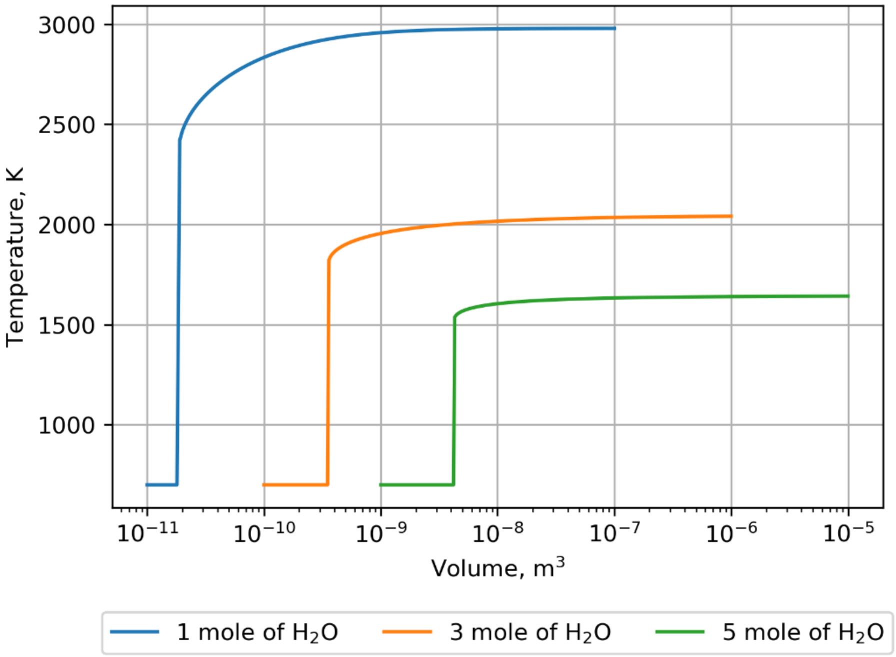

Figure 24 Volumes of the reactors at T_in=700 K and p_in=250 bar.

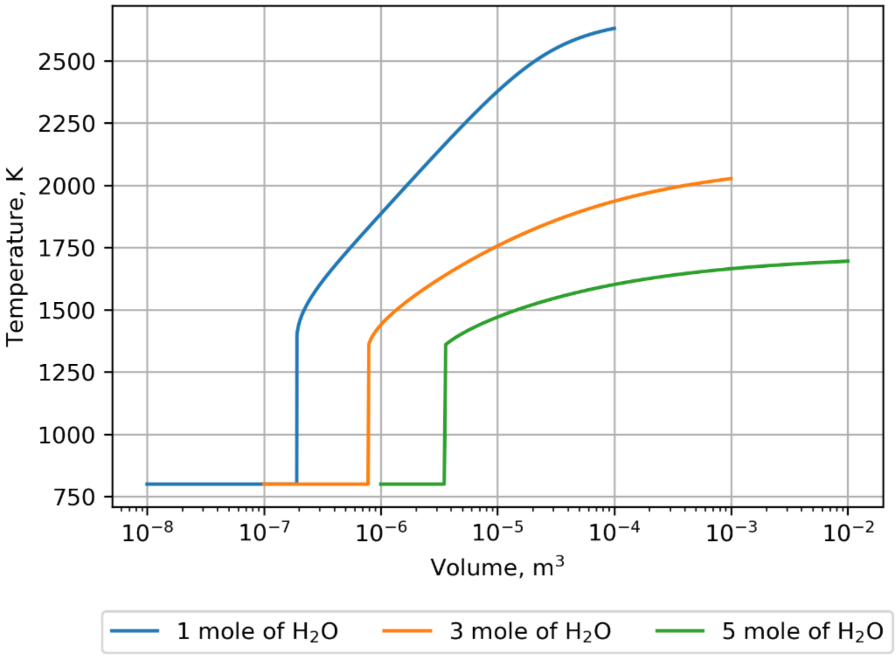

Figure 25 Volumes of the reactors at T_in=800 K and p_in=1 bar.

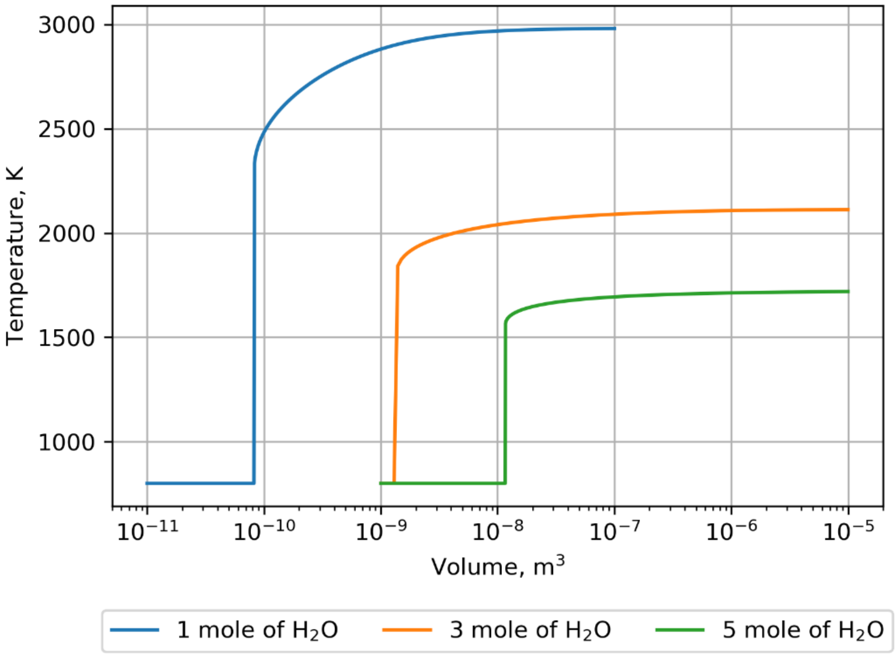

Figure 26 Volumes of the reactors at T_in=800 K and p_in=100 bar.

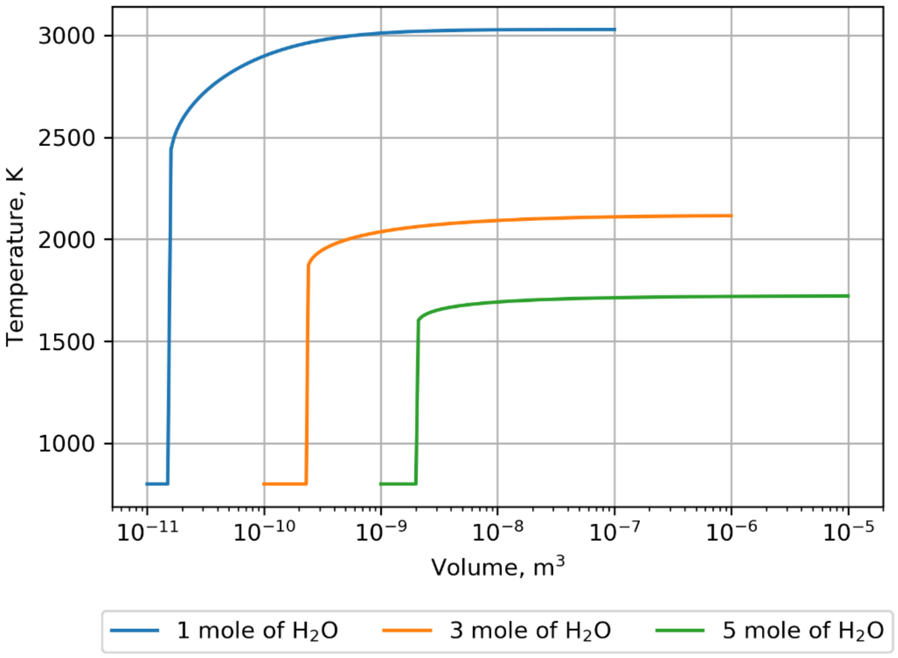

Figure 27 Volumes of the reactors at T_in=800 K and p_in=250 bar.

5.2.2 Influence of residence time on combustion kinetics

The residence time of the mixture in the reactor has great significance in the combustion process. From the definition of residence time it can be understood that it is reservoir volume divide by rate at the inflows or outflows of the reactor at steady state. The residence time in the simulations prepared for the thesis was calculated on the basis of the volume of the reactor.

In the written code in Python for solving the problem, combustion in a well-stirred reactor, the equilibrate function was also used, like in previous calculations, as a preliminary assumption for finding a steady-state composition of reactants. Very important in the conducted calculations is the duration of simulations, within this time the combustible mixture needs to start burning. One more significant aspect of the computation is a time step, which must be small enough to ensure correct run of procedure. If all factors are meet, then the ignition time will be most accurately found.

On the plots in this subsection the residence time values are presented in logarithmic scale which allows easier reading and better presentation of the results. It can be generalized that the time needed for the oxy combustion of hydrogen with dilution of one mole of steam is around 1 microsecond at 100 bars, less than this at 250 bars, and more than 1 μs at 1 bar. With the increase of inlet temperature and pressure the mixture in combustion chamber starts igniting in less time.

Under those same inlet parameters, the minimum residence time after the calculations corresponds to minimum volume of the reactor, this dependence ensures stability inside the combustion chamber.

The cases with the low-pressure (1 bar) at the inlet at all simulated cases in all range of temperature shares this same characteristic of reaching the steady state slowly. This increased time of achieving steady state is most visible when the oxygen is diluted with one mole of H_2O, with the growth of mole fraction of steam dilution the time needed to obtain steady state is decreasing.

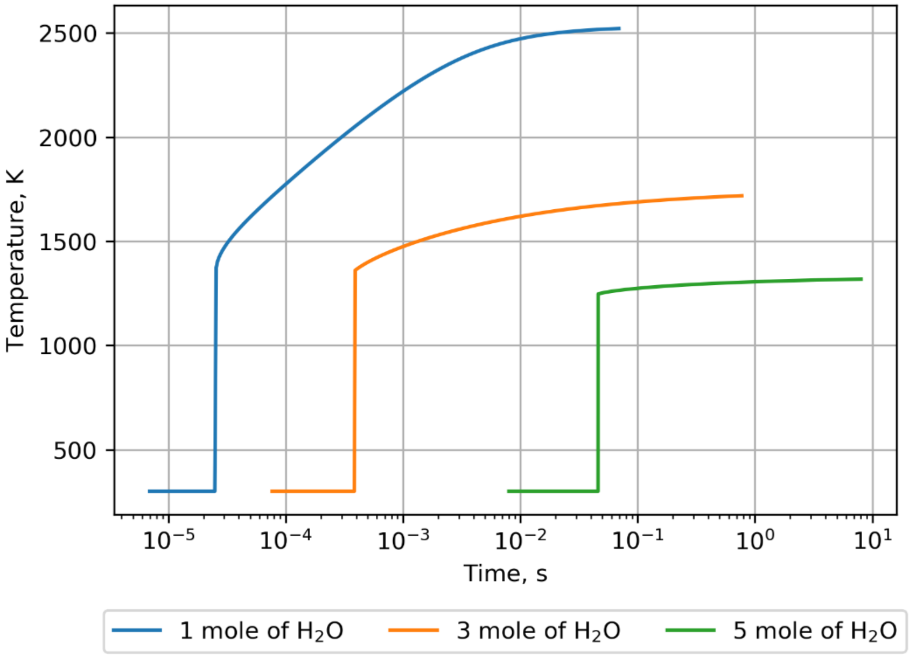

Figure 28 Residence time of the reactors at T_in=300 K and p_in=1 bar.

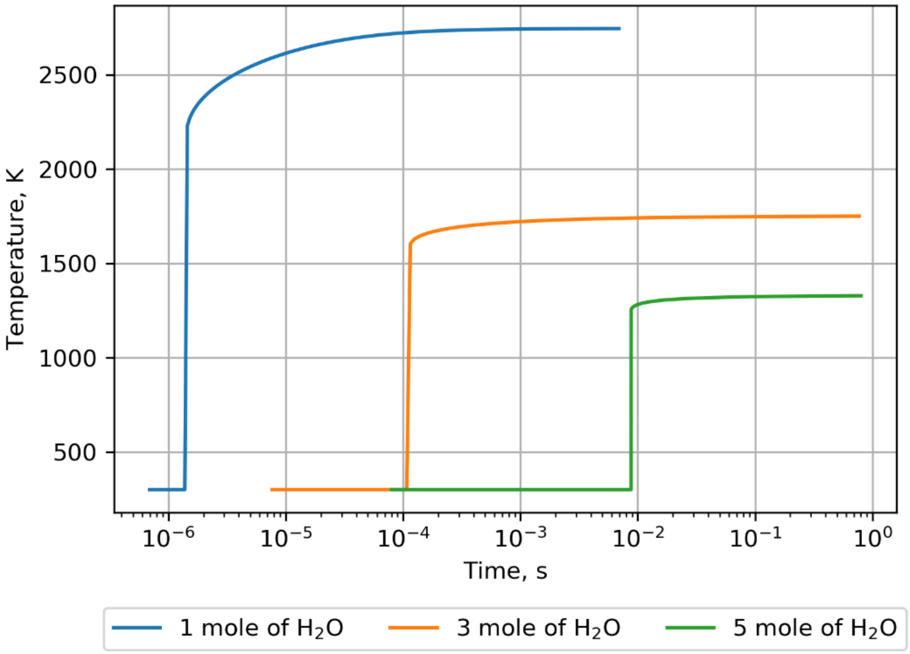

Figure 29 Residence time of the reactors at T_in=300 K and p_in=100 bar.

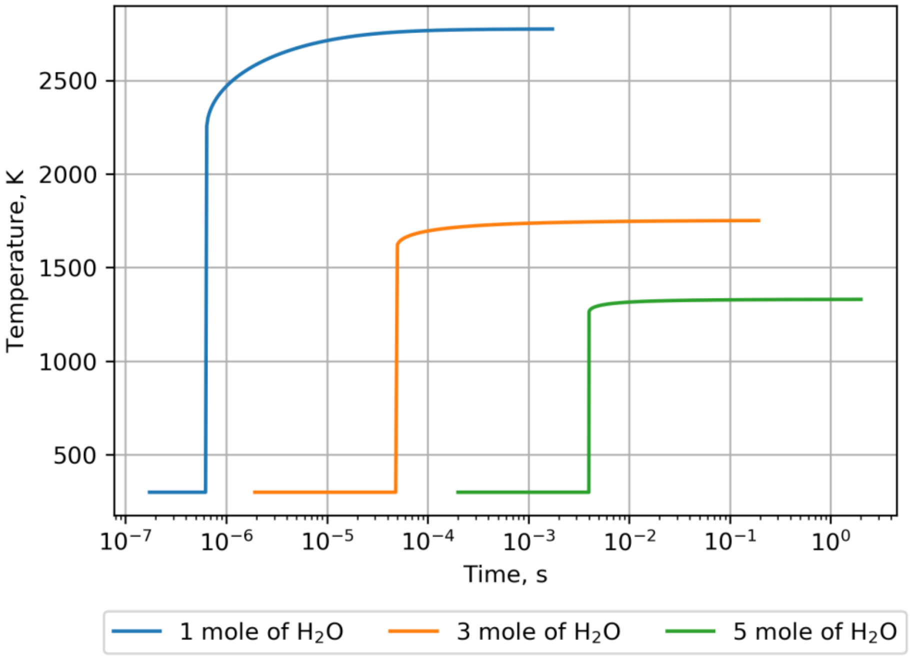

Figure 30 Residence time of the reactors at T_in=300 K and p_in=250 bar.

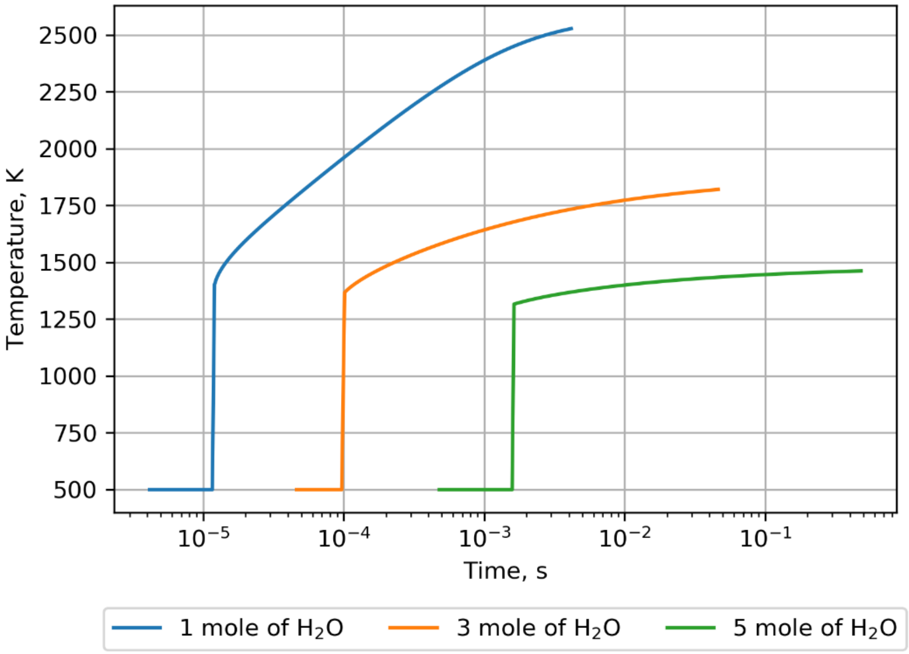

Figure 31 Residence time of the reactors at T_in=500 K and p_in=1 bar.

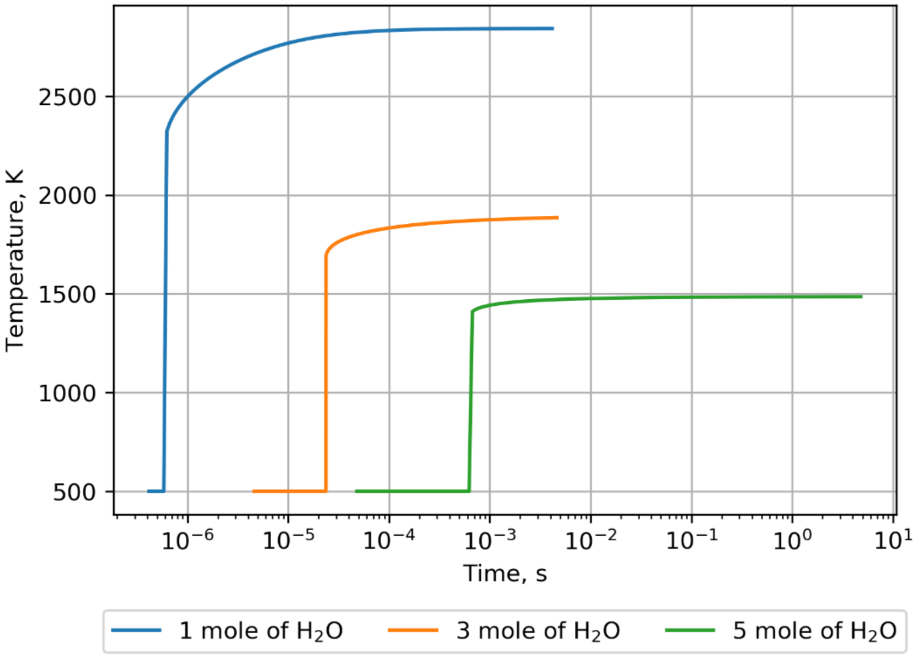

Figure 32 Residence time of the reactors at T_in=500 K and p_in=100 bar.

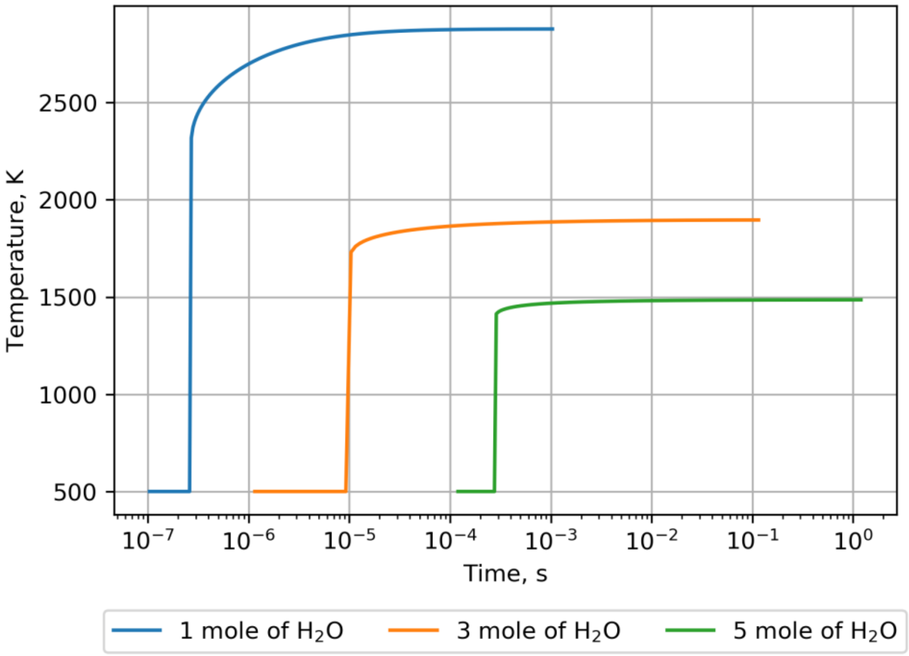

Figure 33 Residence time of the reactors at T_in=500 K and p_in=250 bar.

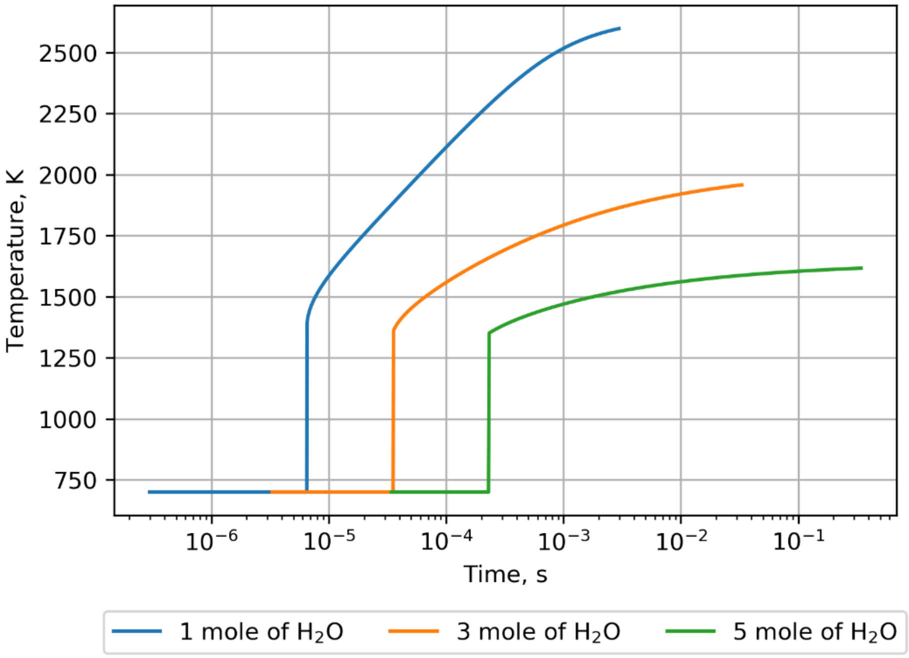

Figure 34 Residence time of the reactors at T_in=700 K and p_in=1 bar.

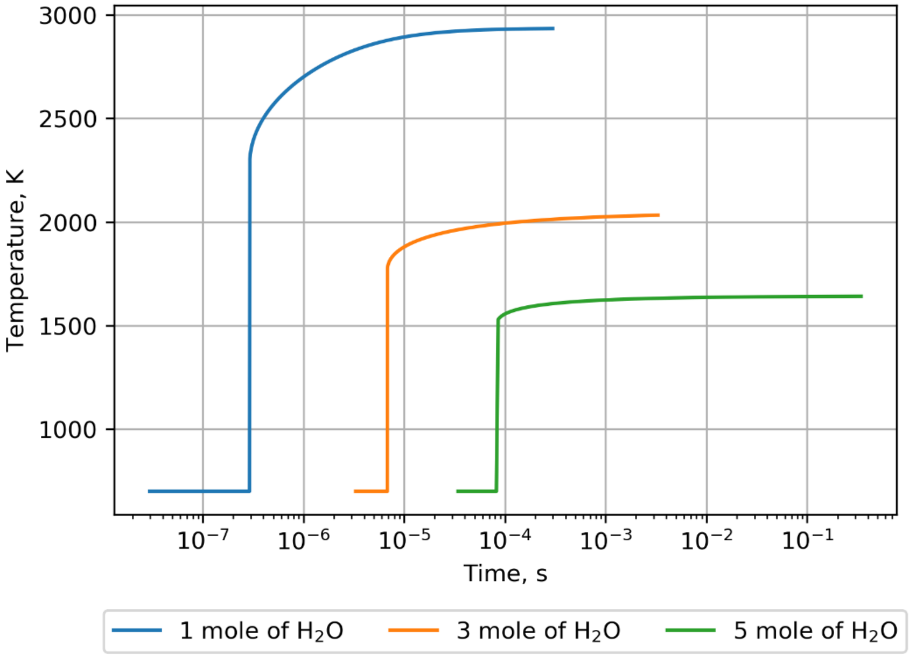

Figure 35 Residence time of the reactors at T_in=700 K and p_in=100 bar.

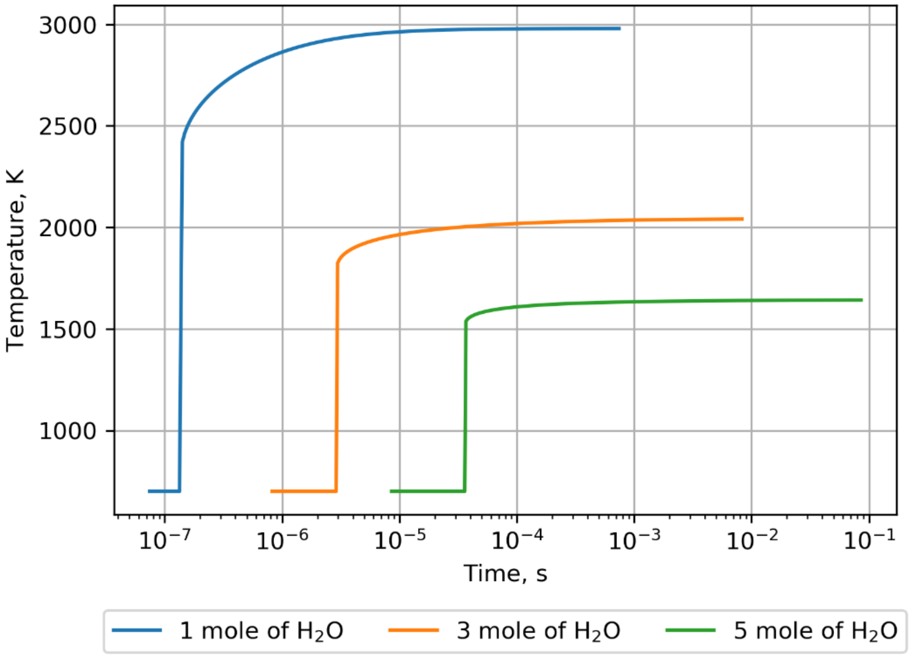

Figure 36 Residence time of the reactors at T_in=700 K and p_in=250 bar.

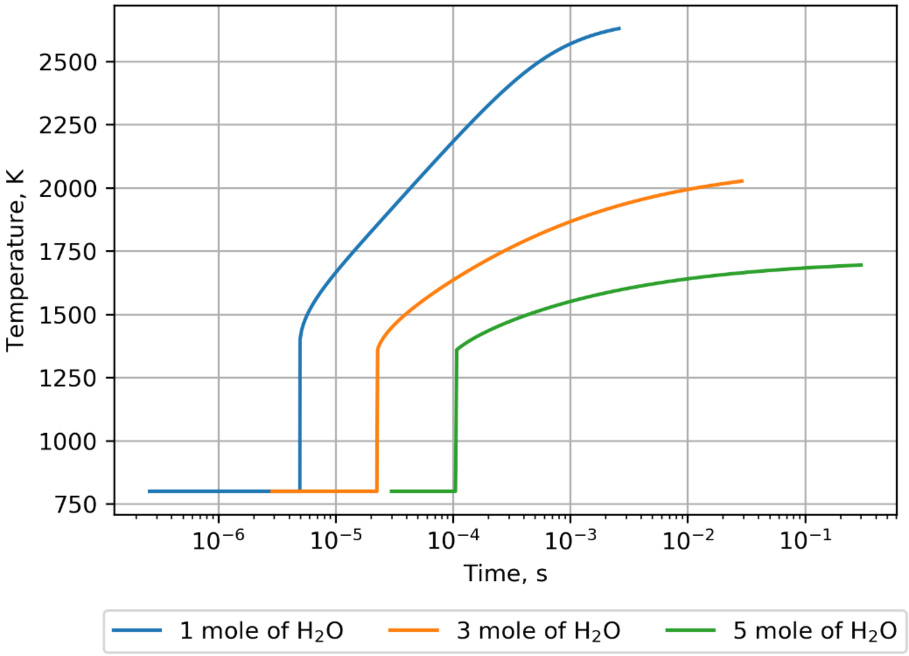

Figure 37 Residence time of the reactors at T_in=800 K and p_in=1 bar.

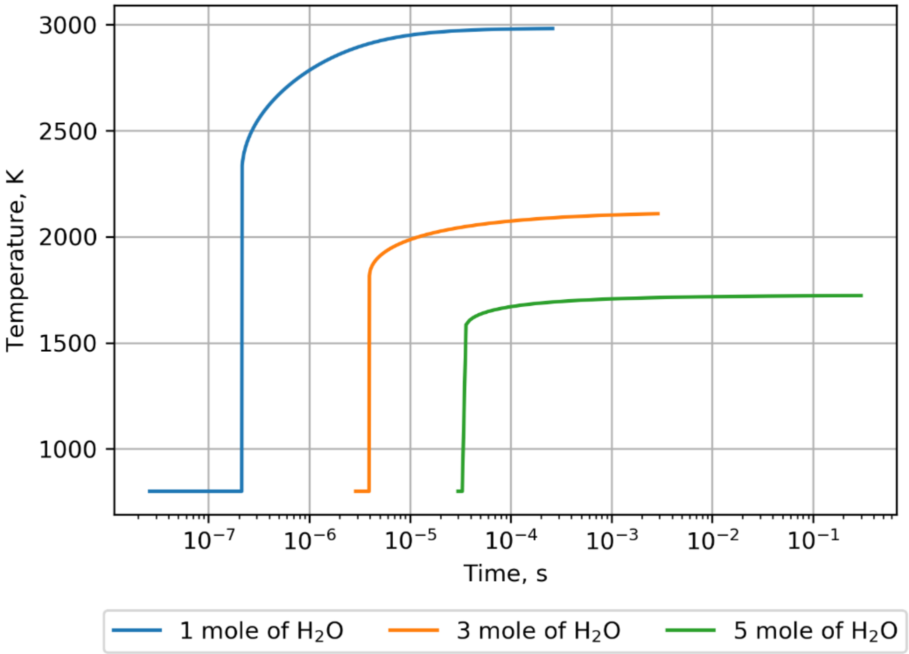

Figure 38 Residence time of the reactors at T_in=800 K and p_in=100 bar.

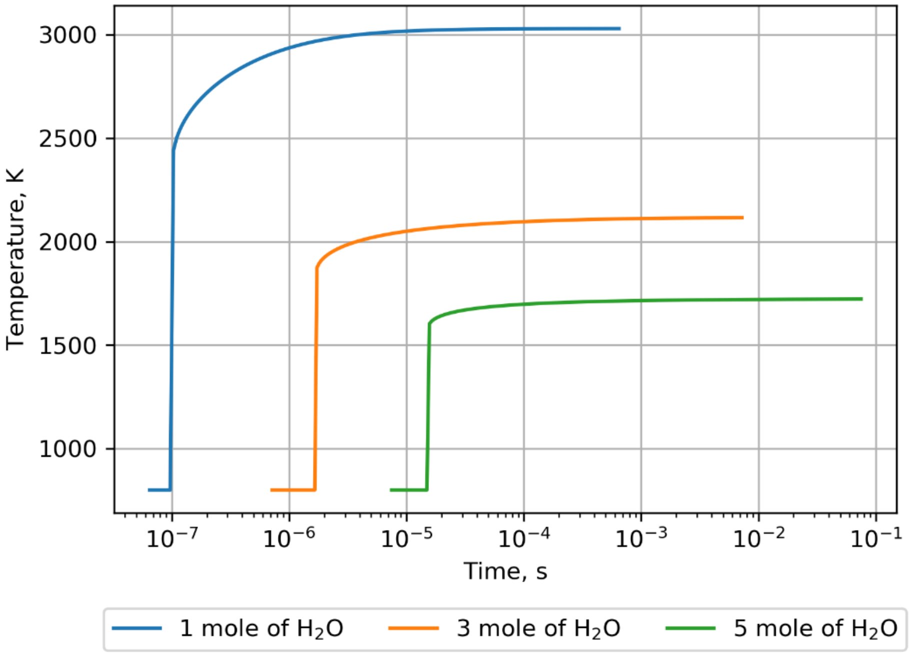

Figure 39 Residence time of the reactors at T_in=800 K and p_in=250 bar.

6 CONCLUSIONS

This master thesis proves the concept that hydrogen can be combusted in oxygen/steam mixtures and this process can be stable and complete. The hydrogen as a fuel has a great potential to become the fuel of the future, with an ongoing worldwide desire for transition in energy field. The steam cycles using hydrogen can be competitive due to its zero CO2 emissions and high efficiencies. The main concern about hydrogen is the cost of production of this gas, but good solution to this is using renewable sources like wind or solar energy. On the other hand, the demand for low carbon gas on the market would in the near future force the policy makers to focus on alternatives of fuel source.

The work in the thesis was divided into three parts: finding an equilibrium composition of hydrogen, oxygen, steam and other species at various pressure and temperature, finding a volume and residence time of reactor oxy-combusting hydrogen. In order to generate and simulate all the reactor combustion or equilibrium composition performed in the thesis, the open-source Cantera software was used, in Python interface, programming language. The results of the conducted calculations, showed on plots in the thesis, present insights into the kinetics of the combustion process.

Implementation of oxy MILD combustion system is a perfect solution for clean combustion of hydrogen, because the gas Is oxidized only in a stream of pure oxygen, so the problem of nitrogen oxides in the exhaust fumes is not existing. The concept of ignition of hydrogen depends on recirculation of the combustion products in the chamber in diluted stream, MILD combustion, this resolves the problem with cooling due to high flame temperature and problem with composition of the outlet stream. It was important in the thesis to find the volume and residence time at which the composition of the gases will be at equilibrium and all hydrogen will react, because the excessive concentration of H2 and O2 at the outlet may auto ignite behind the combustion chamber, which could destroy the condenser or other parts of the cycle.

The obtained outcomes of simulations may be used in future work of model predictions. From the results the design of the experimental facility could be provided. Further steps should include planning and building in ANSYS Fluent a Computational Fluid Dynamics (CFD) model of the experimental facility. The MNRC cycle, reviewed in thesis, should be developed. In the result the simulation of real scale combustors should be possible and verification of the geometry proposed for high, medium and low pressure combusting chambers. The layout of inlets and outlets in the combustor for suppling reactants like fuel, oxidizer and diluted steam and for releasing the products, should be analyzed. When the final configuration of the flow and composition of reactants will be setup than the Large Eddy Simulation technique can be used for the studies, which will reduce the influence of the Reynold Averaged Navier-Stokes (RANS) turbulence modelling limitation. All of this should improve prediction of oxy combustion of hydrogen with dilution of steam and the research combustion cycle could be constructed.

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Appendices

Appendix A

Appendix A includes the equilibrium calculations program written in Python, applied for running the simulations of H_2O. The code from line 35 till 45 is an example of how the plots after simulations were carried out, this case present mole fraction of hydrogen molecules at equilibrium.

```
1.  import cantera as ct
2.  import numpy as np
3.  import matplotlib.pyplot as plt
4.  
5.  gas = ct.Solution('h2o2.xml')
6.  
7.  P = np.array([1,10,50,100,150,200,250])
8.  P = P * (10**5)
9.  T = np.arange(1073,2500,50)
10. 
11. k=0
12. XXH2 = np.ones((len(P),len(T)));
13. XXO2 = np.ones((len(P),len(T)));
14. XXH2O = np.ones((len(P),len(T)));
15. XXH = np.ones((len(P),len(T)));
16. XXO = np.ones((len(P),len(T)));
17. XXOH = np.ones((len(P),len(T)));
18. for p in P:
19.     print(p)
20.     j=0
21.     for t in T:
22.         print(t)
23.         gas.TPX = t, p, 'H2O:1'
24.         gas.equilibrate('TP')
25.         XXH2[k][j] = gas.X[0]
26.         XXO2[k][j] = gas.X[3]
27.         XXH2O[k][j] = gas.X[5]
28.         XXH[k][j] = gas.X[1]
29.         XXO[k][j] = gas.X[2]
30.         XXOH[k][j] = gas.X[4]
31.         j = j+1
32.     k = k+1
33.     print(k)
34. 
35. fig,ax=plt.subplots()
36. k=0
37. for p in P:
38.     ax.plot(T,XXH2[k][:],label=str(P[k]/10**5)+' bar')
39.     k=k+1
40. plt.xlabel('Temperature, K')
41. plt.ylabel('mole fraction $\mathrm{H}_2$, -')
42. ax.legend(loc='upper left')
43. plt.yscale('log')
44. plt.grid(True)
45. plt.savefig('hydrogen.png',dpi=300)
46. 
47. SMALL_SIZE = 9
```

```python
MEDIUM_SIZE = 12
BIGGER_SIZE = 20

plt.rc('font', size=SMALL_SIZE)          # controls default text sizes
plt.rc('axes', titlesize=BIGGER_SIZE)    # fontsize of the axes title
plt.rc('axes', labelsize=MEDIUM_SIZE)    # fontsize of the x and y labels
plt.rc('xtick', labelsize=SMALL_SIZE)    # fontsize of the tick labels
plt.rc('ytick', labelsize=SMALL_SIZE)    # fontsize of the tick labels
plt.rc('legend', fontsize=SMALL_SIZE)    # legend fontsize
plt.rc('figure', titlesize=BIGGER_SIZE)  # fontsize of the figure title
```

Appendix B

Appendix B includes the reactor programs written in Python for simulations of residence time and volume of the reactor under specified inlet pressure and temperature. In given example the 300K and 1 bar case is presented, in others simulation those values were varying.

```python
import numpy as np
import matplotlib.pyplot as plt
import cantera as ct

gas = ct.Solution('h2o2.xml')

inletTemperature = 300
inletPressure = 1*10**5
P = 1
LHV = 120
mdot = P/LHV

H2O = np.arange(1,6,2)
V = np.zeros((3,100000))
V[0][:] = np.arange(0.0000001, 0.0101, 0.00000001)
V[1][:] = np.arange(0.000001, 0.01, 0.0000001)
V[2][:] = np.arange(0.00001, 0.10001, 0.00001)

TT = np.zeros((len(H2O),np.shape(V)[1]))
ttr = np.zeros((len(H2O),np.shape(V)[1]))
jj = 0
for h2o in H2O:
    inletConcentrations = {'O2': 0.5, 'H2': 1, 'H2O': H2O[jj]}
    gas.TPX = inletTemperature, inletPressure, inletConcentrations
    rho = gas.density
    inlet = ct.Reservoir(gas)
    ii = 0
    for v in V[jj]:
        gas.equilibrate('HP')
        reactor = ct.IdealGasReactor(gas)
        reactor.volume = v
        exhaust = ct.Reservoir(gas)
        tr = v*rho/mdot
        ttr[jj][ii] = tr
        pressureValveCoefficient = 0.01
        maxPressureRiseAllowed = 0.01
        mfc = ct.MassFlowController(inlet, reactor, mdot=mdot)
        pv = ct.PressureController(reactor, exhaust, master=mfc, K=pressureValveCoefficient)
        sim = ct.ReactorNet([reactor])
        sim.set_initial_time(0.0)
        sim.advance_to_steady_state()
        tt = sim.time
        gas.TPX = inletTemperature, inletPressure, inletConcentrations
        gas.equilibrate('HP')
```

```
        reactor = ct.IdealGasReactor(gas)
        reactor.volume = v
        exhaust = ct.Reservoir(gas)
        pressureValveCoefficient = 0.01
        maxPressureRiseAllowed = 0.01
        mfc = ct.MassFlowController(inlet, reactor, mdot=mdot)
        pv = ct.PressureController(reactor, exhaust, master=mfc, K=pressureValveCoefficient)
        sim = ct.ReactorNet([reactor])
        t = 0.0
        dt   = tt/100
        states = ct.SolutionArray(gas, extra=['t'])
        states.append(reactor.thermo.state, t=t)
        sim.set_initial_time(0.0)
        while t <= tt:
            t += dt
            sim.advance(t)
            states.append(reactor.thermo.state, t=t)
        n = np.size(states.T)
        T=states.T
        TT[jj][ii] = T.item(n-1)
        ii = ii + 1
    jj = jj + 1



jj = 0
fig,ax=plt.subplots()
for h2o in H2O:
    ax.plot(V[jj][:],TT[jj][:],label=str(H2O[jj])+' mole of $\mathrm{H}_2$O')
    jj=jj+1
plt.xlabel('Volume, $\mathrm{m}^{3}$')
plt.ylabel('Temperature, K')
plt.legend(bbox_to_anchor=(0.5,-0.25), loc='center', ncol=3)
plt.xscale('log')
plt.grid(True)
plt.savefig('300_1Temperature_vs_rector_volume.png',dpi=300, bbox_inches='tight')

jj = 0
fig,ax=plt.subplots()
for h2o in H2O:
    ax.plot(ttr[jj][:],TT[jj][:], label=str(H2O[jj])+' mole of $\mathrm{H}_2$O')
    jj=jj+1
plt.xlabel('Time, s')
plt.ylabel('Temperature, K')
plt.legend(bbox_to_anchor=(0.5,-0.23), loc='center', ncol=3)
plt.xscale('log')
plt.grid(True)
plt.savefig('300_1Temperature_vs_Residence_Time.png', dpi=300, bbox_inches='tight')
```