

Ultra clean combustion, oxy combustion 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 analyze 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.

Keywords: combustion; hydrogen; chemical kinetics; oxycombustion of hydrogen

1. Introduction

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 paper, 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 emission 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. Related work

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 [2] 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. This technology is encouraging because the amount of pollutants, such as nitrogen oxides, can be reduced. This technology depends on dilution of the fuel and air inside combustion chamber without occurrence of flame typical for combustion processes, which means narrow flame front. Modern solutions establish that 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 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. The conception of hydrogen/oxygen steam generators is struggling with main problem of large content of H₂ and O₂ in the combustion products, steam. Those residuals are unreacted subtracts of reaction, which are impossible to avoid, because from [3] 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 advance steam cycle.

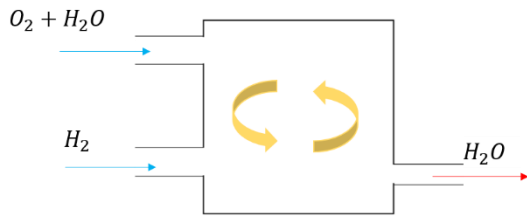


Figure 1 Concept of hydrogen combustion in oxygen diluted steam. (based on [3])

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 [4] 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 [4] 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.

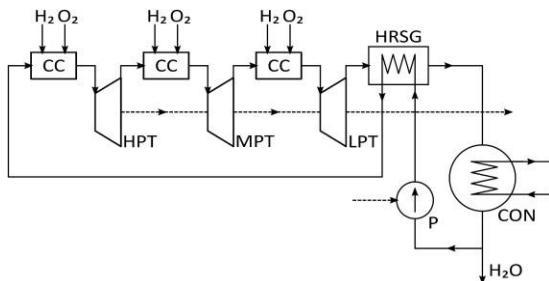


Figure 2 The MNRC cycle (based on [4]), where CON - condenser, P – pump.

Milewski proposed, after analysis of other cycles, in the paper [4] his own concept of the cycle called Modified New Rankine Cycle

(MNRC). Schematic cycle presented on Figure 2 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 H₂O 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 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 is far ahead from fuel cells.

3. Model

This section provides an overview of modelling aspects of the studies performed in this paper. The computational methods carried out with the usage of Cantera software will be described. In order to start computations with Cantera software the kinetic mechanism needs to be selected, for the purpose of this thesis it was the h₂o₂ mechanism. Hydrogen-Oxygen (h₂o₂) mechanism contains 3 elements, 9 species and 28 reactions [5].

The choice of simulation fell on the ideal gas reactor, to be 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 [5]. On the Figure 1 the scheme of the discussed reactor is presented. Chemical reactions inside the perfectly 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 perfectly 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 equations below are used in calculations of perfectly stirred reactor. The summation over the rate equations of all elementary reactions $r=1, \dots, R$ gives the total rate of formation/destruction of a species i . [6] :

$$\dot{\omega}_i = \left(\frac{\partial c_i}{\partial t}\right)_{chem} = \sum_{r=1}^R k_r (v_{ri}^{(p)} - v_{ri}^{(e)}) \prod_{s=1}^S c_s^{v_{rs}^{(e)}}$$

where c_i is the concentration of species $i=1, \dots, S$, and c_s is the concentration of all reactant species in the reaction r other than i and $v_{rs}^{(p)}, v_{rs}^{(e)}$ are the stoichiometric coefficients of the reactant $s=1, \dots, S$, (p) and (e) presents the product and reactant species, and k is the forward reaction rate of reaction r . Species conservation [7]:

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

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.

In the solution described above there may appear a problem with the ignition of the perfectly 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.

The simulation of combustion process 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 presented below:

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

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 [8]. The calculated mass flow rate was then substituted to equation for residence time of the reactor:

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

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.

4. Results

The work in the paper 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. The results of the conducted calculations, showed on plots in the paper, present insights into the kinetics of the

combustion process.

Chemical equilibrium is the state when in a chemical reaction the concentration of products and reactants do not vary in time. 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.

The aim of the equilibrium computations was to determine the composition of H₂-O₂-H₂O system at various conditions. Such computations are useful to predict how much unreacted O₂ and H₂ 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 and the mole fraction and type of the examined

substance is 1 mole fraction of H₂O.

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.

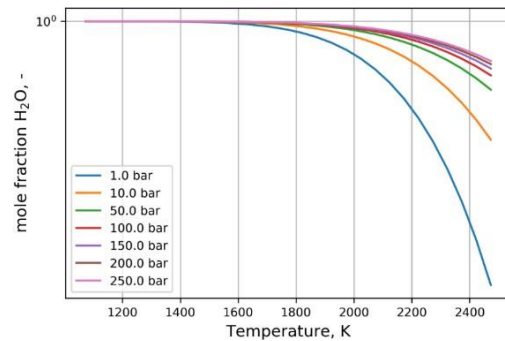


Figure 3 Mole fraction of H₂O at specific temperature and pressure of gas in equilibrium.

The mole fraction of steam, presented on figure 3, 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.

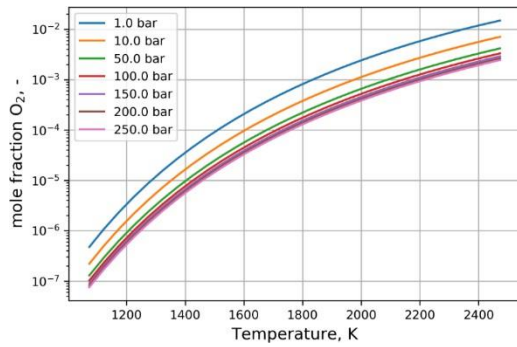


Figure 4 Mole fraction of O₂ at specific temperature and pressure of gas in equilibrium. The mole fractions of oxygen and hydrogen at defined temperature and pressure is presented on figure 4 and 5. In the result of equilibrium simulation those two molecules share the highest mole fraction after the steam mole fraction. The calculated values of O₂ and H₂ 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 H₂ and O₂ concentrations.

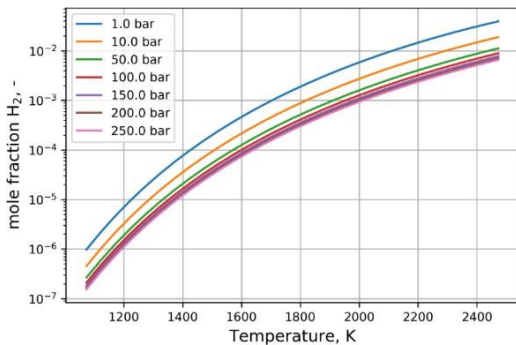


Figure 5 Mole fraction of H₂ at specific temperature and pressure of gas in equilibrium. The case of 1 bar, marked with blue line on the plots, is the low-pressure example in which the mole fractions are the biggest in all examples. When it comes to hydrogen the problem appears in low pressure turbines 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 2, 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.

5. Reactor modelling

In order to mimic the oxycombustion of hydrogen in MILD like mode, the built in Cantera IdealGasReactor model was used. 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 Figure 2, 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 thermodynamic properties presented in Table 1 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 (Fig. 6).

Table 1 Thermodynamic properties

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

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.

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 in Cantera. In order to facilitate the counting, 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 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 the figure 6 till 16 the couple of the chosen results from the simulation are presented. 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 $10^{-7} \text{ m}^3 - 10^{-6} \text{ m}^3$ with one mole of dilution steam
- Volume $10^{-7} \text{ m}^3 - 10^{-5} \text{ m}^3$ with three mole of dilution steam
- Volume $10^{-6} \text{ m}^3 - 10^{-3} \text{ m}^3$ 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. Combustion of hydrogen diluted with one mole of H₂O, independently of inlet pressure and temperature, starts to react at the smallest volume. Therefore, increase of the amount of mole of H₂O in combusted mixture connects unambiguously with increase of the volume needed to start the reaction.

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. 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.

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 μ s 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 H₂O, with the growth of mole fraction of steam dilution the time needed to obtain steady state is decreasing.

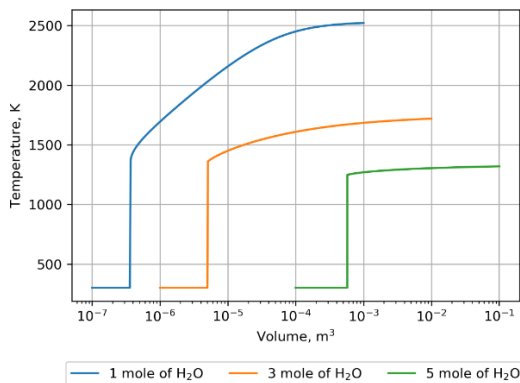


Figure 6 Volumes of the reactors at $T_{in}=300K$ and $p_{in}=1$ bar.

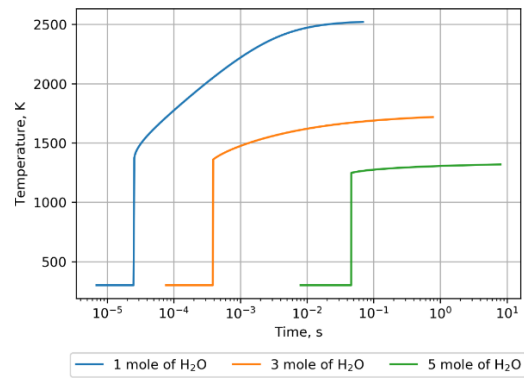


Figure 7 Residence time of the reactors at $T_{in}=300$ K and $p_{in}=1$ bar.

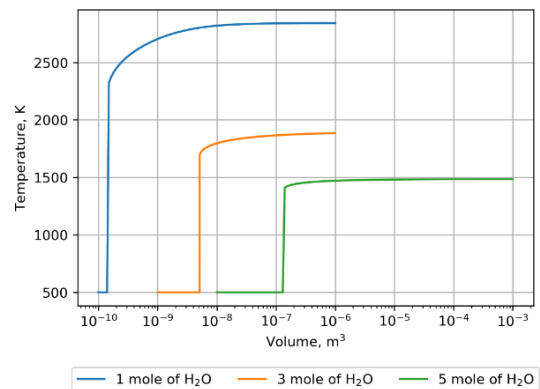


Figure 8 Volumes of the reactors at $T_{in}=500K$ and $p_{in}=100$ bar.

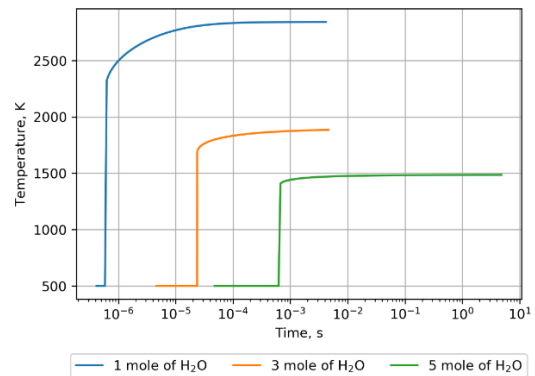


Figure 9 Residence time of the reactors at $T_{in}=500$ K and $p_{in}=100$ bar.

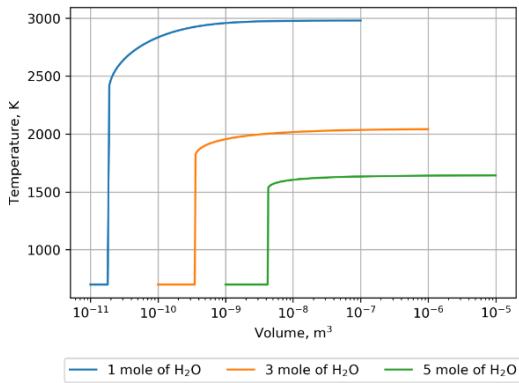


Figure 10 Volumes of the reactors at $T_{in}=700K$ and $p_{in}=250$ bar.

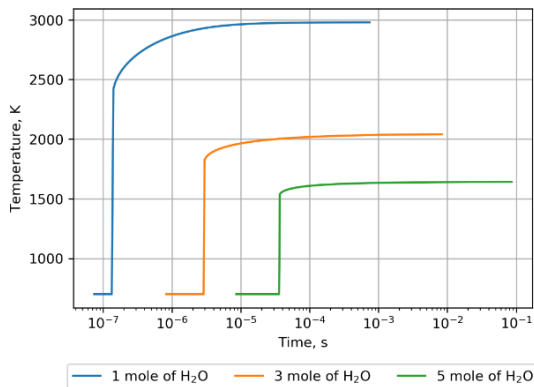


Figure 11 Residence time of the reactors at $T_{in}=700$ K and $p_{in}=250$ bar.

6. Conclusions

Presented paper proves the concept that hydrogen can be combust 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 sun 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.

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 the paper, should be developed. In the result the simulation of real scale combustors would be possible, and verification of the geometry proposed for high, medium and low pressure combusting chambers. 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. 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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