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Hydrogen fuel supply system and re-heat gas turbine combustion

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Abstract

Carbon Capture and Storage (CCS) based on the pre-combustion routine involves a fuel supply and gas turbine combustion system which must handle a fuel with a very high content of Hydrogen. This might cause problems related to ignition and auto-oxidation in the piping in addition to thermo-acoustic instabilities, flash back and increased emissions in the gas turbine. In this work it is found that for typical fuel compositions problems with self ignition and auto-oxidation in the fuel supply system is avoided if the mixture temperature is kept below 400 ºC and the fraction of Oxygen in the fuel does not exceed 3%. Furthermore it is shown that even a reheat combustor can be fuelled with up to 70% Hydrogen and 30% Nitrogen as diluent at full load without problems with combustion instabilities or NOx emissions when inline fuel injection is used together with appropriate mixing devices.

Keywords:CCS; Pre-combustion; Hydrogen; gas turbine; fuel supply

1. Introduction

The international panel on climate change (IPCC) is pointing to carbon capture and storage (CCS) as one of the major paths to keep the global temperature increase by 2010 below two degrees, based on 1990 levels. There are currently three available routes to CCS; 1) pre combustion, 2) post combustion and 3) oxy fuel. All of these routes can be divided into several sub-routes of which all have different potentials and maturity. One of the routes with the highest potential is the pre combustion route utilizing coal in an integrated gasification and combine cycle (IGCC).

In an IGCC syngas is produced by gasification of lignite or hard coal in the pressure range of 25 bar to 35 bar. The composition of the syngas varies depending on the gasified fuel and on the gas treatment. For a pre-combustion CO_2 separation scenario, most of the carbon monoxide is shifted to carbon dioxide which is removed from the syngas. As a result, the main constituents are hydrogen (> 80 % vol), nitrogen (about 10 % vol) and carbon monoxide (about 5 % vol). Additionally, the syngas can include argon (up to

1 %), carbon dioxide (0.5 % vol), and traces of methane. Before this syngas is burned to power in a gas turbine, some additional steps are necessary. The syngas is diluted by waste nitrogen from the air separation unit. This nitrogen may still contain a significant amount of oxygen. Depending on the gas turbine the gas treatment might end here for a lean premixed gas turbine. For diffusion flame gas turbines one may also dilute the syngas with steam.

In the European PF7 project "DECARBit" the focus has been on pre combustion IGCC, and the work presented in the current paper is based on the most significant outcome of the sub-project focusing on the fuel supply system and the combustion process. In section 2 the fuel supply system, with both Nitrogen and steam dilution, is studied. This section is split into three subsections discussing the upper flammability limits, ignition limits and auto oxidation effects, respectively. In section 3 the developments of the second stage burner of Alstoms GT24/GT26 gas turbine, i.e. high hydrogen content re-heat gas turbine without any steam dilution, is discussed and current results are presented. Finally, in section 4, conclusions are given.

2. The fuel supply system

In this section the focus will be on the fuel supply system leading from the CO_2 separation unit to the gas turbine. This includes the sections for dilution with Nitrogen and steam. The aim is twofold; firstly to present design criteria for avoiding potentially hazardous combustion within the fuel supply system and, secondly, to find if significant amounts of fuel may be consumed be parasitic fuel consumption before the gas turbine.

2.1. Upper flammability limits

The knowledge of material safety properties is critical for safe handling when dealing with flammable materials. There is no single parameter that defines flammability, but one that is relevant to gaseous mixtures is the flammability limit. It defines the range of fuel concentrations being necessary for flame propagation to occur. The upper flammability limit (UFL) is the maximum concentration below which the flame can propagate. Flammability limits depend on numerous factors, such as mixture temperature and pressure, presence of inert compounds and oxidant concentration.

Due to the strong increase of reaction rates with the temperature the critical heat release rate is achieved only if the *adiabatic flame temperature* exceeds a certain *threshold value* [1], [2]. Therefore for a set of gas mixtures and initial conditions a direct minimization of the Gibbs free energy is performed in order to obtain the dependencies of adiabatic flame temperature on gas composition and initial temperature. The threshold values of the **C**alculated **A**diabatic **F**lame **T**emperatures (CAFT) are used to determine the flammability limits, and a flammability envelope is constructed.

The threshold values of CAFT for hydrogen are based on the measurements of the explosion limits presented in Schroeder et al. [3]. For gas mixtures threshold values of the CAFT are calculated according to the following mixing rule

$$CAFT_{mix} = \sum v_i CAFT_i,$$

where v_i is the mole fraction of each component of the fuel mixture, and $CAFT_i$ is the threshold value of CAFT for an individual component of the fuel mixture at a certain feed temperature and pressure.

The resulting upper flammability limits are found to increase monotonically with pressure. Furthermore it

is also found that for oxygen concentrations below 3% and temperatures below 400 ºC there is now risk of a propagating flame.

2.2. Ignition limits

In the previous sub section numerical modeling was utilized in order determine if a flame would propagate or not. A more stringent test is to determine if a flame will auto ignite. In the current sub section this is determined experimentally [**4**].

The testing method relies on the ignition of a gas by contact with a hot surface. The gas mixture to be investigated is introduced into a heated test chamber, where it will ignite or not depending on the preset wall temperature and gas pressure. The ignition temperature is considered to be the minimum wall temperature at which ignition is observed.
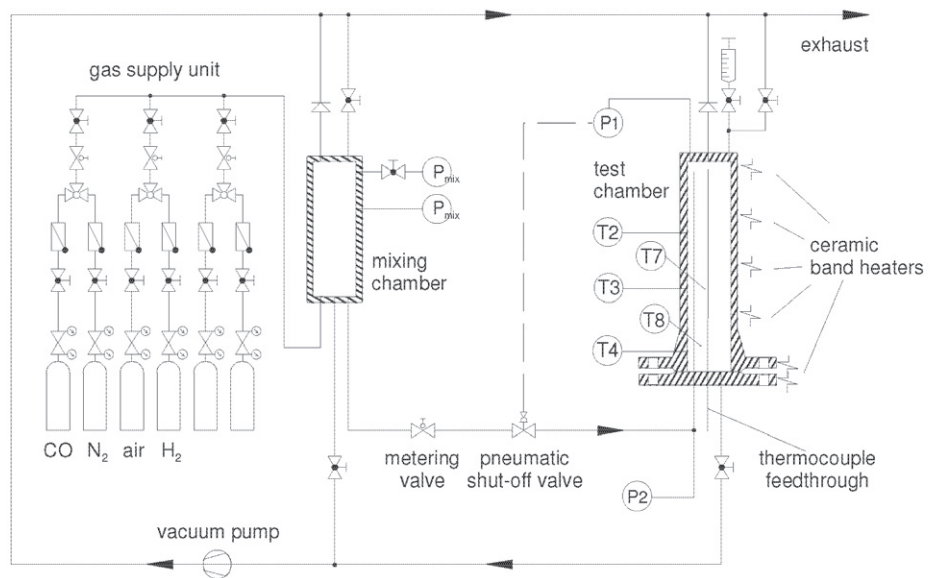
Figur 1: Test apparatus comprising gas supply unit, mixing chamber and test chamber.

The experimental setup comprises a gas supply unit, a mixing chamber and a test chamber. It is shown schematically in Figure 1. Gases such as CO, N_2, synthetic air, and H_2 are stored in gas cylinders. They are selected and introduced into the mixing chamber by a combination of threeway and metering valves which are appropriately combined with non-return and shut-off valves.

The mixing chamber is a stainless-steel vessel with a volume of 1 litre. As it is kept at room temperature auto-ignition of the mixtures to be prepared is unlikely. The pressure inside the mixing chamber is measured by two pressure transducers which cover the range up to 20 MPa.

The test chamber is a cylindrical vessel made of stainless steel with an inner diameter of 79 mm and a volume of 2 litres. It is closed at its bottom by a pair of flanges. Four ceramic band heaters are evenly distributed over the height of the cylinder; two band heaters are attached to the bottom flanges. The heaters are regulated individually; their temperature is measured by NiCr-Ni thermocouples. The temperature inside the test chamber is measured near the wall by three thermocouples, marked T2, T3 and T4 in Figure 1, which are introduced through radial ports.

Two further thermocouples, T7 and T8, are mounted on an axial probe and measure the temperature near the center line of the test chamber. The pressure is registered by pressure transducers P1 and P2 at the top and bottom of the test chamber, respectively

The gas mixtures investigated were intended to model a syngas diluted by the addition of approximately 50 % of nitrogen containing residual amounts of oxygen as an impurity. The mixtures actually used are shown in Table 1. The concentrations of combustibles, H_2 and CO, were kept constant while the oxygen content was varied from 3 to 5 % changing the nitrogen concentration correspondingly. During normal operation of the air separation unit, the oxygen concentration will be much lower (see Table 2) but high oxygen concentration of 3 to 5 % are taken into account here in order to consider possible malfunctions in the air separation unit.

Table 1: Gas mixtures tested

H_2	CO	N_2	O_2
%	%	%	%
46.49	2.45	48.06	3.00
46.49	2.45	47.06	4.00
46.49	2.45	46.06	5.00

The syngas mixtures were exposed to temperatures covering the range from 375 °C to 475 °C at pressures varying from 0.2 MPa to 5 MPa.

The temperature and pressure curves obtained in the ignition tests were classified into three categories defined on the basis of the temperature and pressure:

- ignition with a distinct pulse-like increase in both temperature and pressure
- no ignition, but an elevated wall temperature, $T2 > 500$ °C, for a prolonged period of time and an ensuing high ignition probability
- no ignition, the wall temperature $T2$ constantly dropping after a short initial increase and not exceeding 500 °C for an appreciable period of time.

The results of the ignition tests are summarized in Figure 2. From the figure it is obvious that the mixtures of Table 1 will always ignite above 500 °C. At pressures less than 5 MPa they will most probably never do so at temperatures below 400 °C, irrespective of their oxygen concentration. In the range 400 °C $\leq T \leq$ 475 °C the ignitability depends both on pressure and on oxygen concentration, the ignition probability being highest at high O_2 concentration and high pressure. There are conditions, which during one test may lead to a genuine ignition while in another test there is an elevated wall temperature for a prolonged period of time but no ignition. Hence, from the point of view of operational safety only

events marked by blue symbols should be considered as non-ignitions. Doing so, oxygen concentrations below 3 vol% are considered to be safe.

It needs to be pointed out that the experimental pressure dependences shown in Figure 2 do not agree with those resulting from the calculations of the previous sub section 2.1. This disagreement can be explained as follows: The calculations describe UFLs based on the assumption of a perfectly adiabatic system (no heat losses). They do not care for ignition but only for flammability (that means the ability of a flame to propagate under the conditions investigated).

The experimental conditions deviate from these assumptions in that (a) the combustion bomb does not
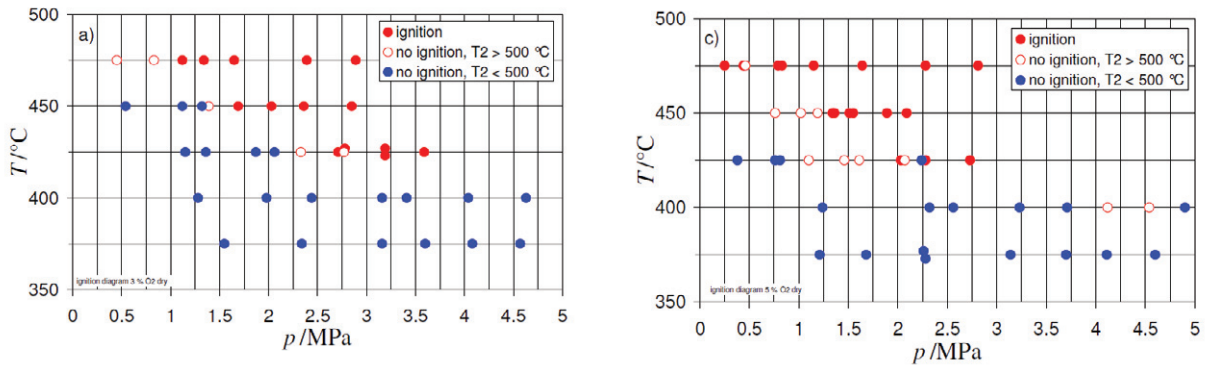

Figure 2: Ignition diagrams for syngas with X(O2)=3% (left hand side) and X(O2)=5% (right hand side). Here *T* is temperature and *P* is pressure.

provide adiabatic conditions and that (b) self ignition is investigated, which means that even if the mixture is flammable ignition may not be observed because the conditions being necessary for self-ignition are not fulfilled.

At a first view this seems to be a simple situation. However, it is not, because under most of the investigated conditions the initiation energy for self ignition has been provided by wall catalytic reactions consuming a substantial fraction of the oxygen within the induction time. Thus except for a few cases with short induction time the gas mixture finally being converted within a very short time (characterized by the rise time of the pressure peak) is not the one fed to the combustion bomb reactor.

Nevertheless, short induction times were only obtained for wall temperatures exceeding 450 °C. For this reason the conclusion drawn already from the ignition diagrams (Figure 2) remains valid: There is no risk of self ignition in the IGCC-CCS fuel system if (a) the oxygen concentration in the diluted fuel is kept at 3 vol% or below and (b) wall temperatures are kept below 400 °C. Since this agrees with the conclusion drawn for the UFL, IGCC-CCS fuel system conditions with oxygen concentrations below 3 vol% and wall temperatures below 400 °C can in general be considered safe.

2.3. Auto oxidation effects

At elevated temperatures, chemical reactions occur when syngas is transported through metal pipelines. In general, these reactions take place heterogeneously at the pipe's surface, while homogenous

reactions do not take place if the temperature is not substantially higher than 350 °C.

For simplicity these reactions will in the following be called auto-oxidation. Auto-oxidation may cause parasitic fuel consumption, corrosion and the plugging of orifices by the deposit of solids. Lab-scale experiments were performed in order to identify the relevant chemical reactions. Moreover, an adequate model is presented that describes these reactions at steady-state quantitatively.

For the evaluation of auto-oxidation effects, only the gas mixture at higher temperatures is relevant, since otherwise the reaction rates are too low. For our evaluation, the composition of diluted syngas given in Table 2 was assumed. The temperature may range from 150 °C to 300 °C, and the pressure can be in the range of 25 bar to 35 bar.

The temperature of 350 °C is too low to expect any homogeneous reactions. However, the metallic surfaces of pipes catalyze chemical reactions heterogeneously. A set of reactions that can describe these auto-oxidation effects is listed in Table 3.

Table 2: Typical composition of diluted syngas

H_2:	42.0 % vol
N_2:	46.0 % vol
Ar:	0.5 % vol
H_2O:	9.0 % vol
CO:	2.0 % vol
CO_2:	0.3 % vol
O_2:	0.2 % vol

For the formation of carbon deposits, two different equations are suggested: equation 3a and equation 3b. For simplicity, only one of these should be considered. Because the concentration of CO is significantly lower than the concentration of H_2, the chemical reaction 3a is more likely to take place. Consequently, it is assumed that the formation of carbon deposits can only take place according to equation 3a, and the well known Boudouard reaction (3b) does not contribute.

Table 3: Set of chemical reactions

Parasitic fuel consumption:		
	3 H2 + CO ↔ CH4 + H2O	(1a)
	H2 + CO2 ↔ CO + H2O	(1b)
	2 H2 + O2 ↔ 2 H2O	
Ammonia and nitric oxides:		
	N2 + 3 H2 ↔ 2 NH3	(2a)
	2 N2 + O2 ↔ 2 N2O	(2b)
	Formation of other nitric oxides	(2c)
Formation of condensed matter		
	CO + H2 ↔ C(s) + H2O	(3a)
	2 CO ↔ CO2 + C(s)	(3b)

Since homogeneous reactions can be excluded at the low temperatures of interest for this study all reactions are related to catalytic activity at the inner walls of the reactor. A model can be defined based on the Langmuir-Hishelwood approach coupled with the classical Arrhenius expression for the rate coefficients. By performing a range of experiments the parameters to be used in the model for the

reactions in Table 3 were produced. In the temperature range of 150 °C to 450 °C and at atmospheric pressure the accuracy of the calculated molar flows is about 10 % in the case of carbon-containing species and substantially better in the case of carbon-free species. The reason for this is the formation of carbon-containing deposits on the reactor's inner surface. Consequently, the history of the reactor can have an influence on auto-oxidation effects which the presented model could not take into account. Under the assumption of first order kinetics the model can be applied for simulation of auto-oxidation effects at high pressure.
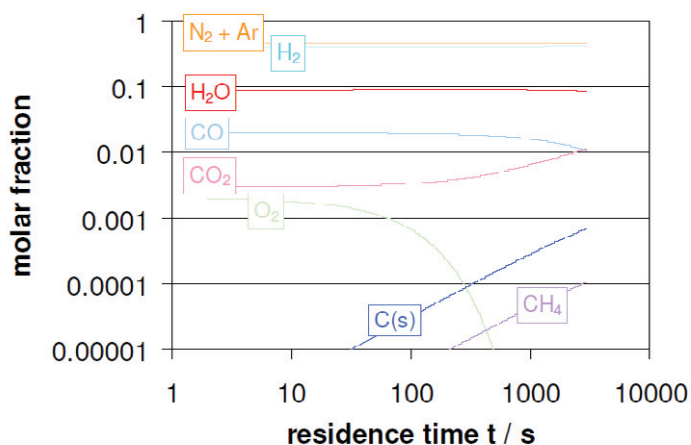

Figure 3: Calculation example of the kinetic reaction model with following parameters: flow rate 1 mol/s, catalytic surface area 1 m2, 350 °C temperature and atmospheric pressure.

Using this model, a simulation was performed giving an example of auto-oxidation effects. The graphs in Figure 3 show the change in composition of the syngas shown in Table 2 as a function of residence time in a piping system or in an experimental reactor. The following parameters were used; a total molar flow rate of 1 mol/s, a catalytic surface area of 1 m^2, a temperature 350 °C and atmospheric pressure.

The trends in the syngas composition explain the influence of the four reactions 1a, 1b, 1c, and 3a. The fastest reaction is the consumption of oxygen that reacts with hydrogen. Since the amount of oxygen is relatively low, this reaction stops if all oxygen is consumed. The next reaction that takes over the regime is the water gas shift reaction. With this reaction, hydrogen is produced while water is consumed. This is why the molar fraction of hydrogen can start to increase again, if most of the oxygen is consumed. Care must be taken at this point: The model accounts only for kinetic effects while thermodynamic effects are not included. For the water gas shift reaction (1b) the equilibrium composition contains significant amounts of all 4 reactants. In this example the molar fraction of hydrogen is about 43.2 % at chemical equilibrium. Because reverse reactions were not taken into account, for sufficiently long residence times the kinetic model would predict hydrogen concentrations being above this chemical equilibrium value.

Therefore in the case of high degrees of conversions kinetic calculations should be substituted by equilibrium in order to avoid such unrealistic effects. However, in a fuel supply system the operation

conditions are far from this point.

Moreover, ammonia was produced only in traces due to the presence of about 2 % carbon monoxide that acts as a catalyst poison for this reaction. However, since the equilibrium composition of a syngas with composition according to Table 2 contains more than 9 % ammonia, the formation of ammonia can become an important reaction at the inner surface of the fuel supply system and cannot be neglected any more for pre-combustion concepts with very high rates of carbon capture.

With the developed kinetic model the reaction rate of carbon deposits per square meter of catalytic surface can be estimated. During the development of the model, it was assumed that all carbon that is missing in the C-balance formed solid deposits of pure carbon. It is also assumed that the reactor is fresh and no deposits are present from previous experiments. This is important, because experimental data confirm that carbon deposits can react to carbon oxides and methane. Consequently, for a long-term run, it is likely that the formation of carbon deposits is balanced by a simultaneous degradation.

Finally; from the model results it can be concluded that for a typical residence time in the fuel supply system of about 4 seconds a fuel mixture containing 3% Oxygen is tolerable as only about 3% of this oxygen will be converted in reactions with the fuel. It should be pointed out however, that for residence times in the excess of a few hundred seconds all the Oxygen will be converted, which clearly is not acceptable. It is therefore crucial that there are no "dead zones" in the fuel supply system where the residence time is significantly longer than the mean.

3. Lean premixed gas turbine combustion

The Alstom GT24/GT26 gas turbine incorporates a unique reheat combustion system [**5**]. Such an approach allows the simultaneous achievement of conflicting operating requirements such as a high firing temperature (for high power and efficiency) and low NOx and increased component life. The GT24/GT26 machines have 2 combustors; the first (EV) combustor is between the compressor and the high pressure turbine, and the second (SEV) combustor is between the high and low pressure turbines. Both combustion systems are based on premixed technology in order to control NOx emissions [**6**].

Since the second combustor is fed by expanded exhaust gas of the first combustor, the operating conditions allow auto ignition (spontaneous ignition) of the fuel air mixture without additional energy being supplied to the mixture. To prevent auto ignition of the fuel air mixture inside the mixing region, the residence time therein must not exceed the auto ignition delay time. This criterion poses challenges in obtaining appropriate distribution of the fuel within the mixing region.

The current SEV combustor is designed for natural gas and utilizes large scale mixing devices to create a complex mixing pattern, into which fuel (both gaseous and liquid) is injected though a lance. This design causes the rapid and uniform mixing of the reactants. As the vitiated air is above the auto-ignition temperature combustion will spontaneously occur after a characteristic ignition delay time depending on the operating conditions and fuel type.

The challenge in utilizing hydrogen rich fuel is principally associated with its reduced auto-ignition delay time, which can be addressed in one of three approaches:

1. de-rating the engine – allowing the same mixing time by increasing the auto-ignition delay time through altering the characteristics of the vitiated air (i.e. the inlet temperature of the flow to the SEV).
2. decreasing the reactivity of the fuel – i.e. by dilution with an inert gas.
3. modifying the hardware – either to reduce the mixer residence time inline with the reduced auto-ignition delay time or develop a concept which is less influenced by the reactivity of the fuel.

Based on the experience gained from developing earlier versions of the SEV burner it is clear that if low NOx emissions are to be achieved then good mixing is required. This is because hot-spots in the combustion zone will increase the amount of thermal NOx production, and the mixing quality is directly related to the amount and magnitude of hot-spots. In previous combustor designs cross flow mixing, where the fuel is injected normal to the main flow, has been utilized. Such an approach is good for maximizing the mixing but suffers from several disadvantages for application to highly reactive fuels:

1. wakes form behind the jet – these can act as flame holders and could significantly limit component life.
2. mixing is highly dependent on the momentum flux ratio – suggesting that significantly different behaviour would be noted for fuels of very different Wobbe indices, as in the case of Hydrogen/Nitrogen mixtures.
3. requirement for high pressure air assist – as this has to be taken from the HP compressor the use of such air is expensive in terms of engine efficiency.

As a consequence of these disadvantages inline injection, where the fuel is injected parallel to the main flow, was selected for the prototype testing. The use of this approach is anticipated to remove the risk of wakes while reducing the pressure drop across the burner. As the momentums of the flows are additive it is anticipated that the burner will function well across a wide range of fuel types, ranging from natural gas to hydrogen rich fuels. It is also believed that lower pressure air can be used to assist fuel injection, which will have significant operational benefits.

However, the use of inline injection has significant implications for both the mixing in the burner and the fuel placement. Since Hydrogen is very reactive it takes too much time to obtain sufficient mixing when using a few large scale mixing devices together with one single fuel inlet. Due to this multiple fuel injection points has been adapted to aid mixing together with a large number of small scale mixing devices.

In order to mitigate NOx emissions one can dilute the fuel with an inert which absorbs heat and thereby lowers the flame temperature leading to less thermal NOx. The fuel is typically diluted with Nitrogen and/or steam. This is however lowering the total efficiency of the plant, and dilution should therefore be avoided. For the work discussed here it was decided to aim for low dilution of only 30 % of Nitrogen and no steam.

Two different combustion setups have been tested; one with a high burner velocity which gives a low residence time in the premixing chamber, and the other one with a lower velocity of the fuel inlet yielding a long residence time. The former is capable of dealing with shorter ignition delay times, but has higher burner pressure drop.

The question then is if the mixing in the high residence time burner is good enough in order to achieve acceptable NOx emissions Full scale single burner high pressure tests have shown that the low residence time burner with a relative inlet temperature of T_{in}= 0.94 gives acceptable NOx emissions for a relative hot gas temperature $T_{HG}/T_{HG,ref} \approx 0.96$. For the high residence time burner the NOx emissions are too high for T_{in}= 0.95, but by de-rating the first burner the emissions are down on the same line as the high residence time burner. By extrapolation and by comparing with the observed trend of the low residence time burner there seem to be indications that for $T_{HG}/T_{HG,ref} < 0.97$ also the high residence time burner will yield acceptable emissions. This means that even for a low pressure drop burner the design fuel of only 30 % Nitrogen dilution will yield acceptable NOx emissions.

4. Conclusion

Two major achievements can be reported from this work 1) requirement for a safe and efficient high

Hydrogen content fuel supply have been found and 2) a lean premixed re-heat burner have been designed and tested at full load with a low dilution fuel of 70% Hydrogen and 30% Nitrogen.

Firstly, regarding the fuel supply system, it has been found that for a typical fuel supply system there are no risk of flame propagation if the temperature is below 400ºC and the oxygen concentration is below 3%. For the auto-oxidation it is found that for typical residence times in the fuel supply system of about 4 seconds and for a mixture with H_2, N_2, H_2O, O_2 and CO only a small fraction of the Oxygen will be converted for Oxygen fractions less then 3%. It is interesting to note that if there is no CO in the mixture the ammonia content would increase drastically. This is because at equilibrium there is typically around 9% ammonia in the mixture but due to the fact that CO acts as a catalyst poison only traces of ammonia is found when CO is present.

Secondly, regarding the reheat combustor design, a premixed re-heat combustor technology has been developed which has demonstrated acceptable NOx levels with a low dilution fuel consisting of Hydrogen and only 30% Nitrogen, while maintaining combustor pressure drop at an acceptable level. Together these two major findings pave the road for a safe and efficient full scale pre-combustion power plant some time in the not too far future.

5. Acknowledgements

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