Consiglio Nazionale delle Ricerche

PROGRAMMA SHORT – TERM MOBILITY – ANNO 2006

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Fruitore:

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Dipartimento: numero di codice

2 Energia e Trasporti

Titolo del programma:

Studio del processo di combustione catalitica ricca ad elevata pressione per l'applicazione in Bruciatori di TurboGas ad emissioni zero

Obiettivi

Progettare e realizzare un studio sperimentale del processo di combustione catalitica di miscele ricche di combustibile (gas naturale) ed aria su sistemi catalitici sviluppati presso l'IRC-CNR, in condizioni di pressioni elevate, di interesse per l'applicazione in bruciatori per Turbogas ad emissioni "single digit" di NOx e CO. Obiettivo propedeutico di breve termine è rappresentato dalla messa a punto delle infrastrutture su scala pilota necessarie alla sperimentazione.

Abstract del progetto

E' stato dimostrato che la tecnologia di combustione catalitica senza fiamma può costituire una valida opzione per la drastica riduzione delle emissioni inquinanti (NOx, CO, incombusti) in bruciatori di Turbine a Gas. In particolare la combustione catalitica di miscele ricche in combustibile rappresenta l'ultima frontiera della ricerca, in relazione alla possibile implementazione industriale. L'ing. Cimino ed il gruppo di catalisi presso l'Istituto Ricerche sulla Combustione del CNR hanno recentemente sviluppato una famiglia di nuovi sistemi catalitici strutturati per applicazioni di ossidazione catalitica ad alta temperatura, il cui impiego è stato già brevettato e licenziato dal CNR per un processo di produzione di olefine (PCT WO 2004105937 del 2004) . Questi nuovi catalizzatori bifunzionali a base di ossidi metallici a struttura perovskitica e ridotti contenuti di metalli nobili, hanno fornito prestazioni superiori allo stato dell'arte anche durante la sperimentazione effettuata per la combustione catalitica premiscelata in bruciatori atmosferici. Tuttavia la possibile implementazione in bruciatori per turbine a gas risulta subordinata ad una verifica delle prestazioni ed ad uno studio approfondito delle caratteristiche di funzionamento in condizioni di pressione superiore a quella atmosferica (fino a 30 atm).
In tal senso presso il Department of Energy Technology, KTH, Royal Institute of Technology – di

Stoccolma in Svezia è stato recentemente allestito un'infrastruttura di ricerca unica nel suo genere in Europa, specificamente sviluppata per la valutazione e lo studio del processo di combustione catalitica in condizioni ultra povere di interesse per bruciatori di turbine a gas. L'apparecchiatura sperimentale è costituita da un reattore su scala pilota con potenza nominale massima di 100 kW (gas naturale), pressione di esercizio fino a 35 atm, preriscaldamento della corrente di aria fino a 600°C e tenore di umidità massimo 30%. Questo tipo di infrastruttura che non è attualmente disponibile presso l'IRC né presso altri centri di ricerca pubblici italiani, richiede un lavoro di aggiornamento e upgrading per essere efficacemente impiegata nello studio del processo di combustione catalitica in condizioni di miscela ricca combustibile aria.

Descrizione delle attività

Le attività svolte dall'Ing. Stefano Cimino durante il soggiorno presso i laboratori KTH di Stoccolma nell'ambito del programma Short Term Mobility 2006 del CNR hanno riguardato principalmente:

- la valutazione e progettazione degli aggiornamenti necessari alle infrastrutture sperimentali esistente per la conduzione delle prove di combustione catalitica in condizioni di miscela ricca,
- la supervisione fase di realizzazione delle modifiche agli impianti, assemblaggio reattore catalitico e taratura apparecchiature
- la definizione della matrice e delle procedure per la conduzione della campagna sperimentale
- la conduzione di un primo set di esperimenti dimostrativi su catalizzatore innovativo specificamente preparato presso IRC-CNR
- la definizione delle raccomandazioni su ulteriori aggiornamenti degli impianti ed apparecchiature necessari al proseguimento dell'attività di ricerca.

Le attività svolte durante il periodo finanziato dal programma short term mobility 2006 del CNR risultano propedeutiche allo svolgimento della campagna sperimentale completa.
Il progetto è stato valutato con grande interesse dall'istituzione ospitante in relazione alla forte componente innovativa dell'approccio proposto (combustione catalitica ricca, finora mai studiata presso il KTH) e del solido know-how acquisito dall'Ing. Cimino sulla preparazione caratterizzazione ed esercizio di reattori catalitici strutturati per applicazioni in ambito energetico e dei trasporti.
In relazione all'interesse dimostrato dal KTH ed agli impegni di ricerca già programmati, si prevede che le modifiche all'impianto sperimentale possano esser implementate antro la fine del 2006 e che la successiva campagna sperimentale per la caratterizzazione del funzionamento del modulo catalitico di combustione ricca in condizioni di alta pressione presso il KTH possa esser completata il primo trimestre del 2007.
Obiettivo di medio termine risulta essere l'estensione della collaborazione scientifica per la realizzazione e caratterizzazione di un dimostratore di combustore catalitico ibrido basato su questa tecnologia innovativa applicata a sistemi turbogas ad emissioni zero.

Fuel Rich catalytic combustion at elevated pressure for ultra low emissions gas-turbine burners

Introduction

Ultra low emissions catalytic combustion of methane under fuel-lean conditions is generally carried out over Pd based catalysts [1,2]. Nevertheless, deactivation at high temperature, the occurrence of large activity hysteresis cycles and strong oscillating behaviours require to limit the catalyst temperature and represent a serious limit to practical implementation of this technology [1,2]. Fuel-rich catalytic combustion has been recently proposed as a preliminary conversion stage for gas turbine burners. In this process a fuel-rich/air mixture is catalytically converted to both partial and total oxidation products which are subsequently oxidized with excess air to complete the combustion in a homogeneous flame [3]. The presence of syngas in the hot product stream from the catalytic zone can help in stabilizing lower temperature flames in the burn-out zone, thus reducing NO_x emissions [4]. In this case the limited extent of the catalytic reaction, due to the poor oxygen availability, prevents the catalyst from reaching high temperatures even in the presence of a not perfectly mixed feed, thus avoiding catalyst deactivation and significantly improving its durability [3]. Moreover, the absence of adsorbed surface oxygen under fuel-rich conditions minimizes catalyst volatilization as noble metal oxide [3].

It has been demonstrated that catalytic partial oxidation of methane can yield near complete conversion to mostly H_2 and CO at reaction times as short as 1 ms in structured catalytic reactors running autothermally, entailing dramatic reduction in reactor size and complexity [5-7]. Several studies have reported that catalysts with high Rh loadings (5-15% w./w.) onto ceramic foam monoliths and honeycombs provided the best performances compared to Pd and Pt based systems in terms of lightoff temperature, H_2 yields, stability against volatilization, resistance to carbon deposition [3,5,6]. On the other hand less studies have focused on the influence of support material and its interactions with the noble metal on catalyst performance, especially under operating conditions of interest for real application [8,9]. In particular, it was reported that irreducible oxides promote the formation of active Rh metal sites more than reducible supports [10] and that the use of hexaaluminates as Rh supports resulted in lower syngas yield and lower stability than α-Al_2O_3 [11]. On the other hand, we have recently found that the strong synergy and interaction existing between noble metals (Pt, Pd) and a perovskite support ($LaMnO_3$) led to enhanced catalyst performance in terms of activity and stability at high operating temperature both in the lean catalytic combustion and the oxidative dehydrogenation of light hydrocarbons [12,13].

On the basis of such results, in this work Rh/$LaMO_3$ (M = Co or Mn) alumina supported structured catalysts have been developed and tested for the oxidation of methane/air mixtures under fuel-rich conditions. The addition of the perovskite oxide has been proposed in order to better disperse Rh and reduce its required amount by stabilizing it in a wide range of temperatures and, at the same time, to promote both the full oxidation and reforming reactions, thus reducing lightoff temperature, enhancing methane conversion and inhibiting coke formation [14-16].

Surprisingly, despite much interest over the last decade and extensive development of this technology by the major petrochemical companies, such as Shell, Exxon-Mobil, ConocoPhillips, only very limited work on high pressure fuel rich catalytic oxidation of methane has been reported in scientific literature. Furthermore, in these works testing at very small scale, augmentation with steam and CO_2 or exotic catalyst structures, such as honeycombs made of fused Rh foils, were used, making the results only indirectly applicable to practical applications of the CPOX process.

Motivation

1. Develop a catalytic combustion technology that addresses the limitations of previous catalytic combustion technology.
   Potential advantages of Fuel rich Catalytic Combustion
   - capable of high-firing-temperature operation
   - with well-controlled catalyst temperatures, over a wide operating range
   - tolerant to wide variations in inlet temperature and F/A ratio
   - of compact size & low pressure loss (no preburner, relaxed mixing requirements)
   - fuel flexibility operation.
2. Enable DLN gas turbines to deliver robust single digit emissions with minimal modification / retrofit. Catalytic pilot replaces diffusion flame/partial premixed pilot. Catalytic reaction provides stability to the pilot flame, which in turn provides stability to swirler flame.

Objective

Final aim of this work is to demonstrate robust, steady-state, operation of a methane CPOX reactor at high pressures (up to 1.5 MPa) testing the novel catalyst formulations developed at IRC-CNR in order to assess operability windows and study the effect of main parameters on reactor performance. Cooperation with KTH in Sweden offers the chance to obtain experimental results in one-of-a-kind facilities in Europe allowing for robust evaluation of this innovative combustion technology under operating conditions of interest for real application in Gas Turbine combustors with Ultra Low Emissions.

DURATION

A 3 week period was spent by Ing. Stefano Cimino (IRC-CNR) from 12/05/2006 to 02/06/2006 at the KTH laboratories in Stockholm in order to setup and start the experimental campaign on the high pressure catalytic reactor test rig after necessary modifications and upgrading necessary to cope with fuel rich/catalytic partial oxidation approach. Catalyst development and engineering was preliminary carried out at the IRC .

Description of Activity

Catalyst preparation and characterization

The novel bi-functional Rh-perovskite catalyst for the experimental campaign at the KTH laboaratories were prepared and characterised at the IRC-CNR in Naples.

Commercial cordierite monoliths (NGK) with square channels and a cell density of 600 cpsi (hydraulic diamerter d_h=0.96mm), were first cut in order to obtain cylindrical samples (d=30mm, l=9-18mm) , which in turn were coated using a modified dip-coating procedure with a thick La_2O_3 (~7% w./w.)-stabilised γ-Al_2O_3 layer and finally calcined in air at 800°C. Rh and perovskite precursors were deposed on the stabilised alumina washcoat through impregnation with an aqueous solution of $La(NO_3)_3 \cdot 6H_2O$ (Aldrich, >99.99%), $Co(NO_3)_2 \cdot 4H_2O$ (Aldrich, >99%) or $(CH_3CO_2)_2Mn \cdot 4H_2O$ (Aldrich, >99%) and $Rh(NO_3)_2 \cdot 2H_2O$ (Fluka, purum.). The samples were dried in MW oven and in stove at 120°C and calcined at 800°C for 3 h under flowing air. The process was repeated 8 times in order to achieve the target loading (~30%w./w. perovskite and 1%w./w. Rh with respect to the active washcoat layer, monolithic substrate excluded). In the following, catalysts will be labelled as LMR.

Specific surface area of active layer after repeated calcination at 800°C was lowered to roughly 70 m^2/g compared to ~200 m^2/g of the starting submicronic γ-Al_2O_3 powder, due to the introduction of the different active phases components.

SEM/EDS analysis showed a good adhesion of both support and active phase and a uniform distribution of La and transition metal into the alumina washcoat, whereas Rh penetration was limited to a surface layer <10μm.

Fig.1 a shows one of the LMR catalytic samples before mounting inside the experimeltal rig at KTH. During fuel rich combustion experiments at KTH laboratories the catalytic monoliths were stacked between two inert radiation shields (mullite foams, 45ppi) and tightly sealed in a alumina tube that was inserted in the stainless steel pressurised reactor vessel. Catalyst wall temperatures were measure by means of K-type thermocouples (d=0.8 mm) positioned inside a closed channel of the monolith (tip at 3 mm from exit section) , in close contact with the solid, and in the exit gas just after the catalyst (Fig.1 b).

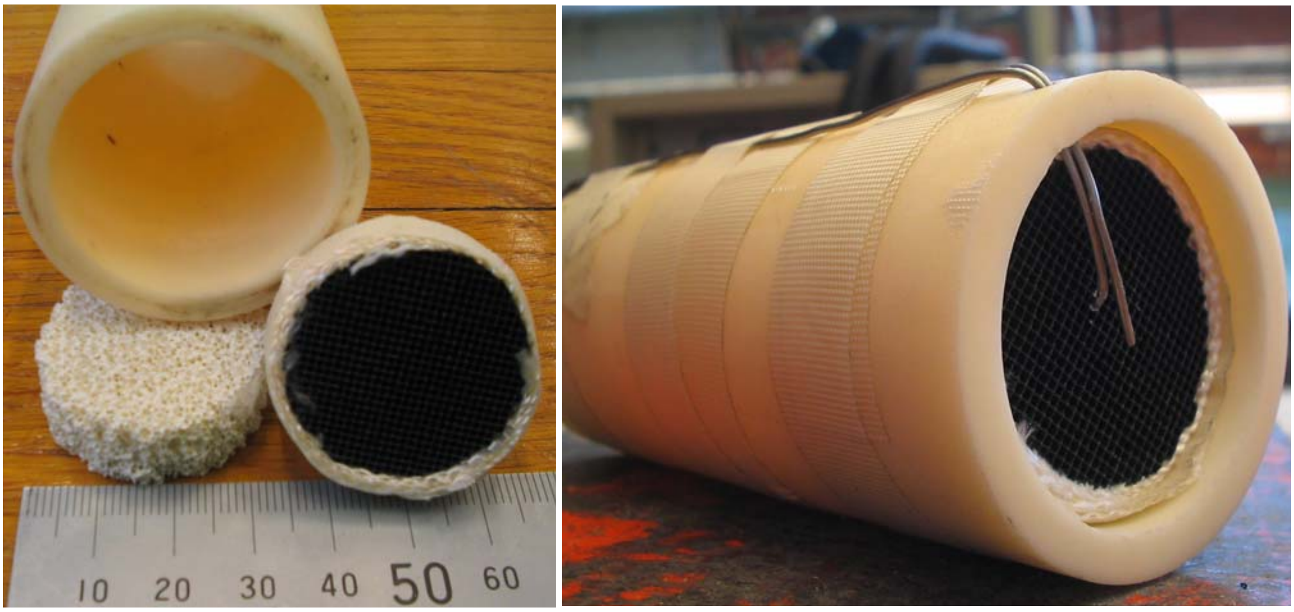


Figure 1 a) LMR catalytic reactor prepared at IRC-CNR (600cpsi, d=30mm, l=8mm) and blank foam monolith (mullite 45 ppi) used as heat shield and static mixer in front of the catalyst. b) close-up of the catalytic module inside the alumina tube instrumented with k-type thermocouples (d=0.8mm) for solid wall and gas temperature measurements.

Catalyst	**Cell density** (cpsi)	d_h mm	**D** mm	**L** mm	**Active layer** g; (%wt.)	**Nominal Composition % wt.** [a]			**B.E.T.**[a] m²/g
						La/γ-Al_2O_3	**$LaMnO_3$**	**Rh**	
LMR	600	0.96	18	11	0.91 (50.4)	69.95	29.1	0.95	68.4
1	600	0.96	30	8	1.72 (49.3)				
2	600	0.96	30	9	1.89 (49.7)				
3	600	0.96	33	9	2.47 (49.1)				
4	600	0.96	30	18	3.91 (49.3)				

[a] referred to the weight of active layer, monolithic substrate excluded

Table 1– Catalysts denominations, shape, active phase content, nominal composition and specific surface area. LMR is a reference sample. Fuel rich catalytic combustion test at KTH were performed on sample n.1.

Major Hardware of the Test Facility

The construction of the test facility is an integration of three main specific sub units, such as high pressure air supply, compressed air humidification system and pressurized catalytic combustion system. Other sub sections of the test facility are compressed air preheating and control system, fuel supply and control system, temperature measurements system, emission collection and analysis system and computer assisted data acquisition and control system. The figure 2 gives an overview of the overall design of the existing test facility at KTH. The overall design of the rig was mainly carried out for testing the premixed catalytic combustion of methane (or gasified biomass) under very lean conditions, characterized by adiabatic temperatures of the mixture not exceeding 1200°C (corresponding to $CH_4 < 4\%$ in air).

It is clear that operation under fuel rich conditions requires important modifications of the experimental set-up and procedures. Major part of the 3-week period spent by Dr. S. Cimino at the KTH the experimental rig was dedicated to the disassembling, inspection of main elements and parts, mounting of catalytic elements, assembling and instrumentation of the reactor.

In the following the main parts of the existing rig will be described, highlighting the implications and issues connected with fuel rich operation of the system.

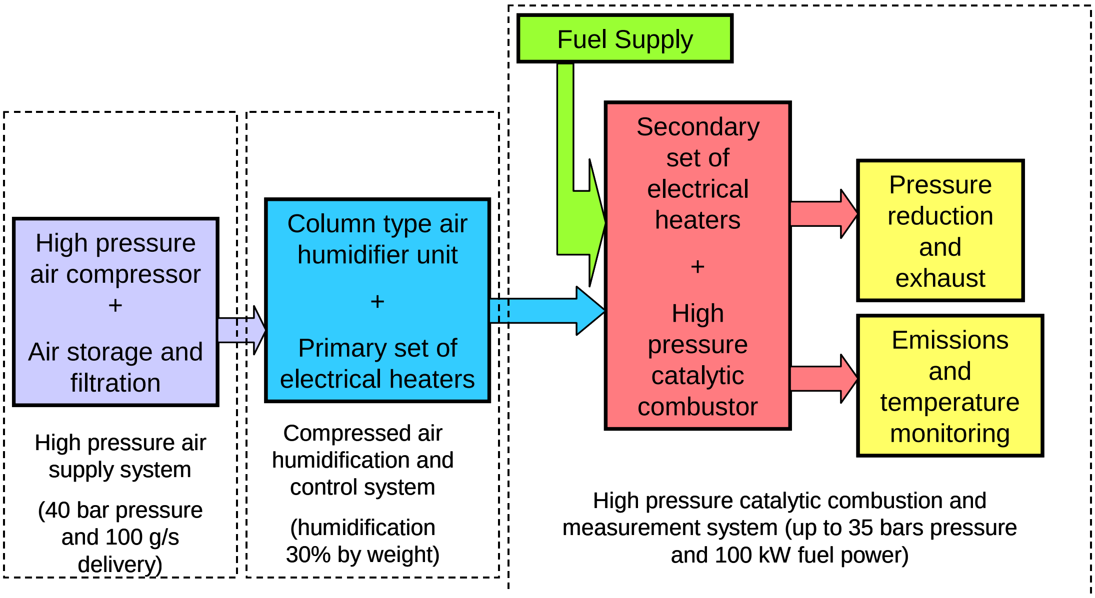


Figure 2 Overview of the experimental facility

High Pressure Air Compressor and compressed air supply system

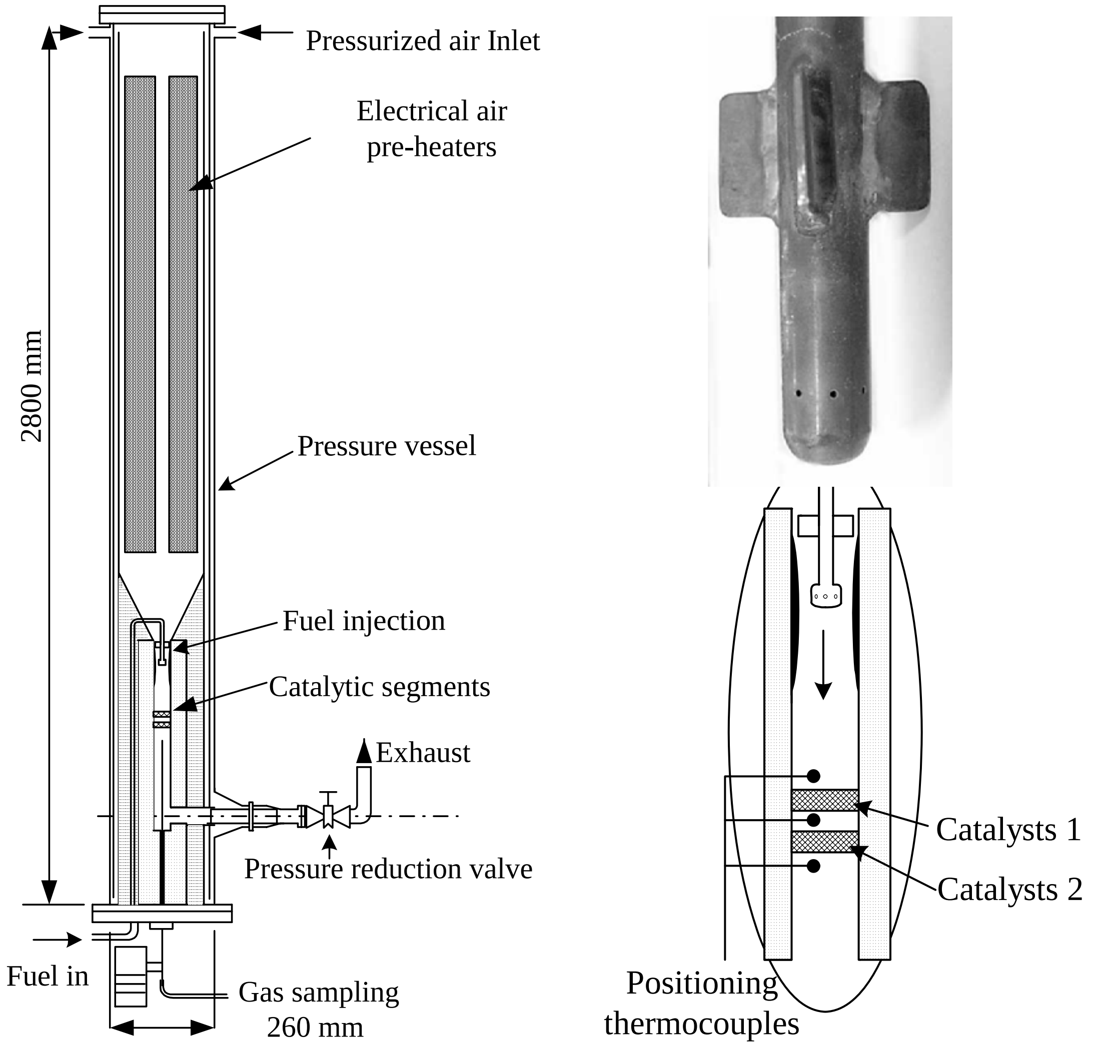
The test facility is supplied with compressed air by a high-pressure stationary type air compressor. The 40 bar, two stage reciprocating type compressor employed for this task has a delivery capacity of 100 g/s. The compressed air supply system is connected with other standard components such as air reservoir tank and filters. The capacity of the tank is 1000 liters and the pressure is maintained at 35 bars. There are three main adjustable components to set the pressure and flow through the combustor. The pressure regulator installed at the entrance to the humidification column basically sets the pressure and the electronically operated flow regulation valve placed just after the pressure regulator controls the air flow at specified rate. The third component, the back pressure valve placed at the exit of the high pressure vessel also plays a crucial role in maintaining set pressure and flow conditions. It must be noted that both pressure regulating valves are manually operated and therefore cannot be easily controlled in order to change operating pressures avoiding large flow oscillations.

For fuel rich operation the required air flow at the catalytic section is proportionally reduced to 70-80% vol. of the total flow. Indeed this implies that for a fixed nominal power input the required airflow is reduced by a factor 10. In this case it is the fuel flow rate rather then air flow that becomes the limiting factor for setting operation window of the rig.

High Pressure Catalytic Combustion unit

Figure 3 shows the design of the high pressure combustion unit. A cylindrical chamber of 3 meters of height and 300 mm in diameter, pressure vessel contains the 2 meters long bunch of electrical heaters hanging at the top of the vessel. The combustion chamber, which is placed at the bottom of the vessel is only 550 mm long. The purpose of the long heaters is to obtain uniform temperature profile across the air-flow. The 80 kW heaters are operated and controlled electronically in order to maintain required temperature levels at the inlet to the combustor.

The "can type" combustor of 550 mm height and 35 mm in diameter is well insulated with high temperature insulation materials and the combustion is expected to occur near adiabatic conditions. The combustor length consists of 200 mm mixing length and 350 mm reactor length. The fuel injection is done at the entrance of the 550 mm long combustor tube. A cylindrical type fuel injection head with eight radial holes is placed on the axis at the upstream of the combustor can.



(a) (b)

Figure 3 a) Schematic diagram of the pressurized combustor. b): **Enlargement of catalytic section and fuel fuel injection head**

The mixing tube takes the shape of veneturi where the fuel injection holes are placed at the minimum cross section of the duct. The high turbulence created by the geometry at the fuel injection points enhances the air fuel mixing in the duct.

The catalytic combustor takes the simple geometrical shape as a straight tube with a total length of 300 mm and diameter of 35 mm. The total length is made up with three pieces of ceramic tubes. These ceramic pieces are serving as catalyst holders. The ceramic holders are then placed inside the cylindrical casing made of high temperature insulation materials. This arrangement has certain advantages as a test combustor. It provides easy access to catalytic elements and convenient to change elements according to different configurations. The piecewise ceramic structure avoids the risk of thermal cracking. The ceramic liner is consisted of number of ceramic rings placed on over the other and merged into the inner hole of cylindrical liner, which is made of high temperature insulation material.

Figure 4(a) shows the bottom part of the high pressure rig, where the catalytic tube in installed. Figure 4 (b) shows the assembly of catalytic combustor section into the high pressure rig while Figure 4 (c) shows a picture of pressure vessel mounted with catalytic combustor test section.


(a) (b) (c)

Figure 4 Combustor and high pressure vessel

Since there is no turbine connected to the test facility, hot exhaust gases at high pressure should go through a pressure reduction device before dump to the atmosphere. A specially designed water-cooled pressure reduction (figure 5) valve is employed for pressure reduction and safe release of exhaust gases, which then go through a silencer to the atmosphere.

The operational capacity (fuel power supplied) of the test facility is determined according to combustion pressure of interest. In order to maintain a constant level of residence time in the combustor at each test condition (at varies combustion pressure) Compressed air mass flow rate into the combustor has to be increased. Consequently the fuel power supply has to be increased to maintain the air fuel ratio at required levels (λ value).

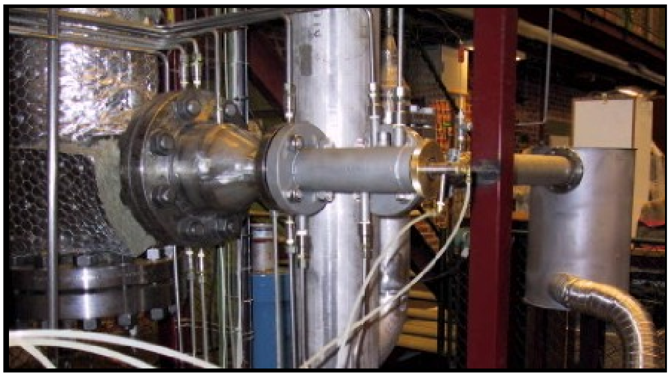


Figure 5 Manually operated back pressure reduction valve

Fuel supply Injection and Mixing

A group of mass flow controllers of different flow capacity were installed in parallel to control the fuel flow. By means of the computer based control system, a corresponding flow controller is triggered to control the fuel flow.

The inlet duct of the combustor takes a venturi shape at the point of fuel injection. The arrangements accelerates the air flow at the fuel injection point to higher flow velocity. At higher flow velocity, turbulence makes better mixing.

Due to the strong reduction in the airflow under fuel rich operation, mixing and preheating of the feed mixture to the catalyst section may represent a serious challenge to be addressed. In fact mixing can be enhanced by placing refractory foam monoliths in front of the catalysts which act as static mixers (at the expenses of increased pressure drops throughout the combustion chamber). On the other hand the fuel flow cannot be preheated inside the reactor, and this will cause a sensible temperature reduction especially at high input power, due to the strong cooling effect connected to the lamination of methane from high pressure bottles (up to 200 bar) to the operating pressure of the rig.

Measurement System

The measurement system is implemented for the on-line measurements of pressure, temperature, flow rates and concentrations of emissions. The instruments are communicating with software controlled data acquisition system and data are stored in 1 Hz frequency.

Pressure inside the combustion chamber is monitored through the signals from pressure transducers installed at the entrance to the high pressure combustion chamber with a nominal accuracy of 0.1% of the measured value.

The compressed air flow into the test facility is measured by digital mass flow meter[1]. The flow meter, works on the Coriolis principle [Fransson, 1995] to measure mass flow directly so, the measurements are unaffected by changes in fluid density, pressure, viscosity and temperature. This makes extremely good accuracy of the air flow measurement which has to be done at varies operating pressures under test conditions. According to the manufactures specifications [Danfoss, 1993], the measurement accuracy of the system is within ±0.15% of actual flow (measured).

Fuel flows are set and measured by mass flow controllers (MFC). They provide the function of mass flow measurement and the control. Up to four mass flow controllers of different capacity, 2.5, 25, 63 and 97 kg/hr flow capacities (as air equivalent) are connected in parallel to minimize the uncertainty of the measurement of the fuel flow.

Several K-type thermocouples are employed on the test facility for temperature measurements. The temperature measurements from the combustor section are extremely important to map reactions in each area. Thermocouple positions in the combustor are at the bulk temperature of the inlet air stream, bulk stream temperature at inlet and exit of each catalyst and the on the surface of catalyst

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[1] Danfoss Flow Instruments, MASSFLO® flow meter: Sensor type MASS 2100/Signal converter type MASS 3000.

monoliths. Thermocouples with two sizes of sheath diameter are chosen for this instrumentation. Thermocouples placed for bulk flow stream temperature measurements are 1.6 mm diameter and thermocouples placed for catalysts surface measurements are 0.8 mm in diameter.

A set of single component on-line gas emission monitoring system was implemented on the test facility. Table 7.1 lists the species that were set to monitor with the respective measuring range of the equipment, accuracy and the measuring principle.

Species	**Measurement range**	**Resolution / Linearity**	**Measurement Principle**
O_2	0-5/25%	≤1% F.S. linearity	Electrochemical
CO_2	0-1/16%	≤1% F.S. linearity	NDIR
CO	0-50/2500 ppm	≤1% F.S. linearity	NDIR
CO	0-1/15%	≤1% F.S. linearity	NDIR
H2	0-1/15%	≤1% F.S. linearity	TCD
CO	0-50/2500 ppm	≤1% F.S. linearity	NDIR
THC	$0\text{-}10/10^2/10^3/10^4/10^5$ ppm	±1% F.S. linearity	FID
NO	$0\text{-}10/10^2/10^3/10^4/10^5$ ppm	±1% F.S. linearity	Chemilumin
NO_2	$0\text{-}10/10^2/10^3/10^4$ ppm	±1% F.S. linearity	Chemilumin
NO_x	$0\text{-}10/10^2/10^3/10^4$ ppm	±1% F.S. linearity	Chemilumin

Table 2 On line emission analysis instruments

The high range CO and H2 analysers were specifically added for the fuel rich experimental campaign. In fact some major limitation with the available instrumentation are related to the unreliable measurement of unconverted methane in the presence of molecoular H2 in the product mix , and to the not-specific measurement of H2 which is strongly affected by the interference of CH4 and CO2.

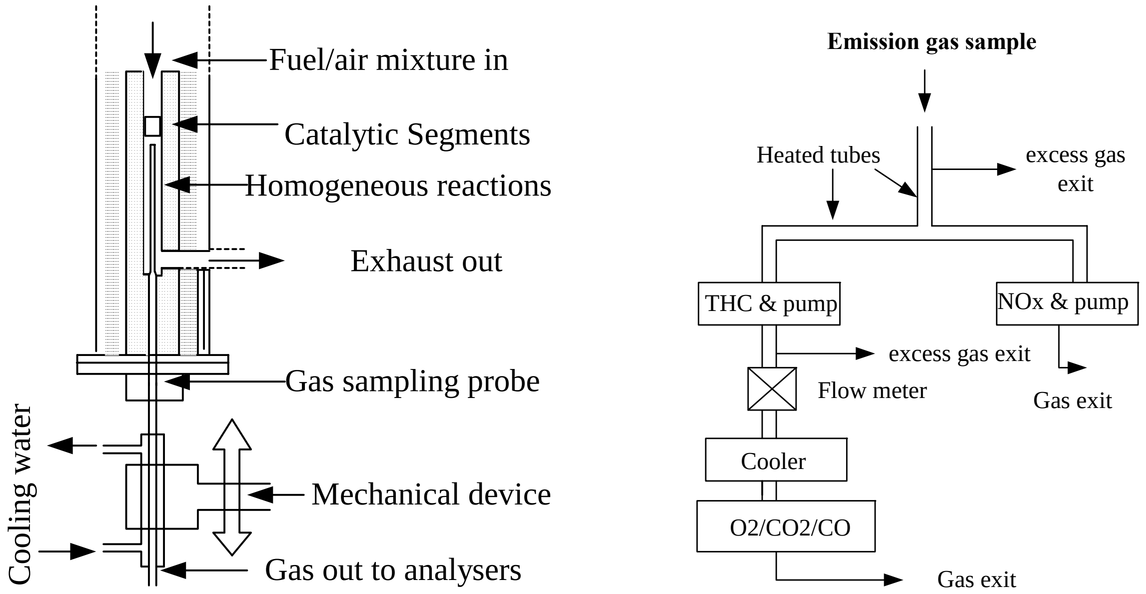


Figure 6 Positioning of traversable water-cooled gas sampling probe and Arrangement of emission analysis instruments.

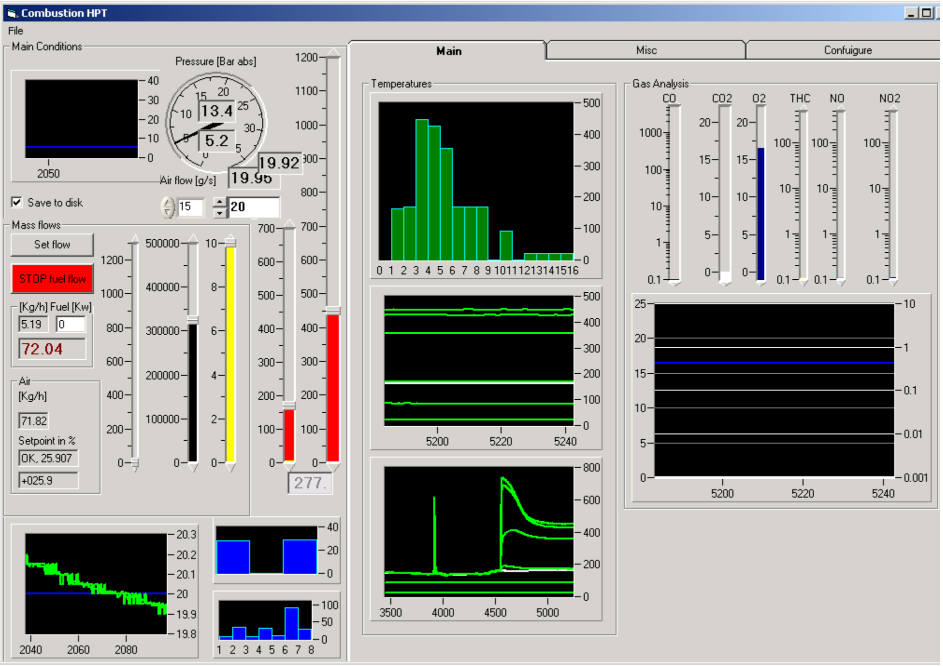
The emission samples are collected by means of a traversable gas sampling probe. Which gives the possibility of collecting samples at different zones in the combustor. The probe is a special design manufactured for the use of high pressure rig. The water-cooled sampling probe was made out of high temperature steel. The dimensions of the probe are 900 mm long in length, 1 mm diameter in gas suction path and 6 mm in external diameter. Co-axial cylinders of cooling water channels take the space between gas suction path and the external housing. The water-cooled probe gives the advantage of quenching chemical reactions and the information of radicals and incomplete products are available to analysis system. The cooling water supplied to the probe is kept under pressure (20 bar) to avoid boiling and to ensure sufficient flow rate through tiny coaxial channels. Figure 6 show the positioning of sampling probe in the high pressure test rig.

Data Acquisition and Control System

The data acquisition and control system implemented on this test facility is in house built control software. The main software program was written under visual basic program and linked several commercially available control software for communicating measuring instruments as sub routings. The graphical display capabilities of labview (a commercial software) are used for buildup user interface on visual basic. The control system has totally 140 data acquisition and control channels. Eighty channels out of the total are accessed through data logger (where A/D conversion is done) while the rest are connected to the computer through Ethernet or RS 232 connections. The channels allocated for the measurements are as following:

- Temperature measurements
- Pressure measurements
- Air flow measurement and control
- Fuel flow measurement and control
- Emission measurement

Figure 7 shows the user interface of the control program. The interface graphically displays the real time values of the temperature variations across the catalysts, surface of the catalysts, inlet and exit air temperatures, emission levels, fuel flow rate and the space velocity. The values indicate numerically are value of combustion pressure, set and operating values of the air and fuel flow rates.



☑ Save to disk

[Kg/h] Fuel [Kw]
5.19 0
72.04

Air
[Kg/h]
71.82
Setpoint in %
OK, 25.907
+025.9

Figure 7 Computer interface – data acquisition

Results of exploratory test run

The first set of experimental data on fuel rich catalytic combustion of methane over novel bi-functional Rh-LaMnO3 structured catalyst developed by IRC-CNR were obtained by running a series of exploratory tests on the high pressure combustion rig installed at the KTH in the configuration already described. The experimental conditions chosen for the start up and the range of operating parameters explored are reported in Table 3. Briefly, the experiments were carried out at fixed pressure (slightly above 5 bars), input thermal power (i.e. methane flow rate, equivalent to 20 kW) and preheating of the air flow. From this point, the flow of air was varied in order to explore the effect of the feed ratio CH4/O2 on the performance of the system: consequently, the residence time and GHSV were during the run. It must be noted that the conditions chosen were representative of a real gas turbine combustor and very demanding for the catalytic section, in particular with respect to the residence time which was as low as 3 ms at the highest flow rates.

	Starting conditions			**Range of variation**
Input Power	**20**	kW		**Fixed**
CH$_4$	**0,025**	mol/s		
	0,399	g/s		**Fixed**
	36,6	slpm		
Pressure	**5,2**	atm		
CH$_4$/O$_2$	**1,7**			**1,1 ÷ 2,1**
Air	**0,07**	mol/s		
	2,02	g/s		**1,64 ÷ 2,05**
	103	slpm		
Total flowrate	**2,33E-03**	Nm^3/s		
	139,5	slpm		**120 ÷ 196**
Combustor Diameter	**3,50E-02**	m		**Fixed**
Cross Section	**9,62E-04**	m^2		**Fixed**
Linear velocity	**0,47**	m/s	at RT	**0,41 ÷ 0,65**
Catalyst Volume	**6,01E-06**	m^3		**Fixed**
Reidence time	**1,14E-02**	s	at RT	**8,1E-03 ÷ 1,33E-02**
	3,17E-03	s	at 800°C	
GHSV	**1,39E+06**	h^{-1}	at RT	**1,96E+06 ÷ 1,20E+06**
	5,02E+06	h^{-1}	at 800°C	

Table 3 Initial set of operating parameters and range of variability explored during the test run on fuel rich catalytic combustion.

Figure 8 reports the temporal evolution of the main operating parameters (Temperatures of gas and catalyst, Flow rates, Pressure and feed ratio CH$_4$/O$_2$) as measured during the test run.

As a general feature it appears that the point of view of the operation of the experimental rig the main and unsolved issue is the control of the air flowrate. In fact, the pneumatic activated control valve is not really capable of assuring a constant flow of air due to the relatively low flow when operating under fuel rich conditions. This circumstance is made more complicated by the presence of a manually operated pressure control valve: once the pressure valve is set on a fixed position, the pressure inside the vessel rises with the total flowrate, thus continuously affecting the control system of the pneumatic valve, which in turn has a rather limited rangeability. The same kind of problem arises when trying the change the pressure by operating the valve at the exit of the reactor at fixed flow-rate.

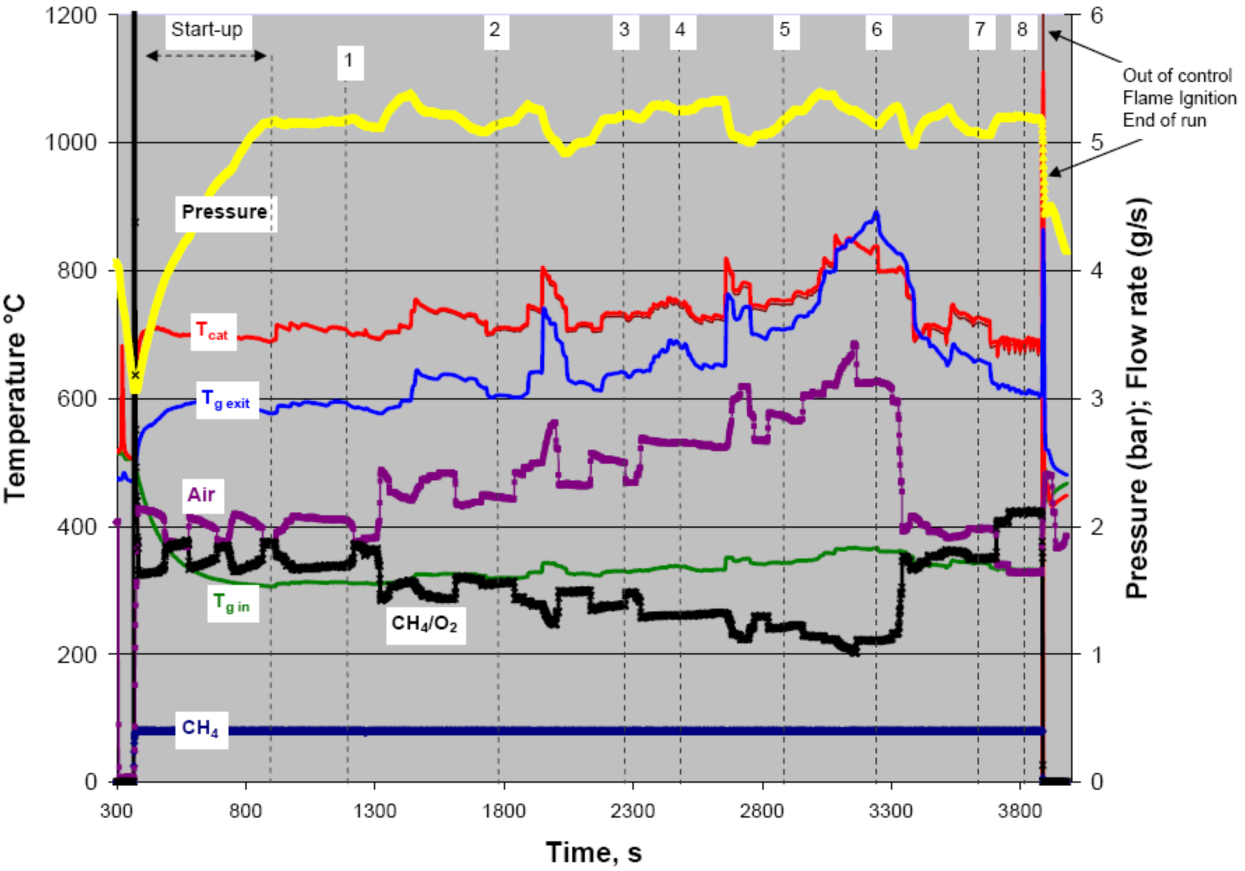


Figure 8 Temporal evolution of main operating parameters during test run of high pressure fuel-rich catalytic combustion over Rh-LaMnO3 catalyst.

Prehaeting of the inlet mixture is actually obtained only by heating of the air flow, wheras the methane flow arrives very cold at the injection port due to the absence of a specific heat exchanger. As a consequence the temperature of the gas mixture entering the catalytic section (Tg in) decreases as soon as methane is admitted to finally stabilize at around 320°C, from thereon being slightly affected by the variation of air flow. Under normal operation the temperature of the catalyst surface is the highest recorded in the entire combustor (Tcat), and is followed in close contact (a few °C below) by the temperature of the gas measured just a few millimetres after the catalytic module, indicating a therma equilibrium between the gas and the solid surface at the exit of the monolith. This also implies that the all the exothermal reactions occur on the surface of the catalyst.
On the other hand the temperature measured in the gas downstream of the catalytic module (Tg exit) follows the trend of Tcat but is normally lower by as much as 110°C due to heat losses and eventually to the possible occurrence of endothermal reactions (ie methane steam and dry reforming). Only at the lowest value of feed ratio CH4/O2 =1.1, corresponding to the higher total flowrates explored, the situation reverts, with Tg exit exceeding Tcat (condition 6 in Figure 8). In

this case part of the oxygen appears to skip unconverted the catalytic monolith, so that some exothermal homogeneous combustion occurs downstream of the catalyst and heats the gas.

Figure 9 shows one of the main feature of the rich catalytic combustion system is the strong correlation axisting between the operating temperature of the catalyst and the feed ratio CH4/O2. In fact the catalyst surface temperature can be easily controlled by setting the appropriate fuel to air ratio, preserving the long term stability and durability of the active phase by avoiding exposure to temperatures in excess of 1000°C. It is also evident that increasing the air flowrate (i.e. decreasing the CH4/O2) the reaction tends to be partly blown outside of the catalyst because of the reduced residence time.

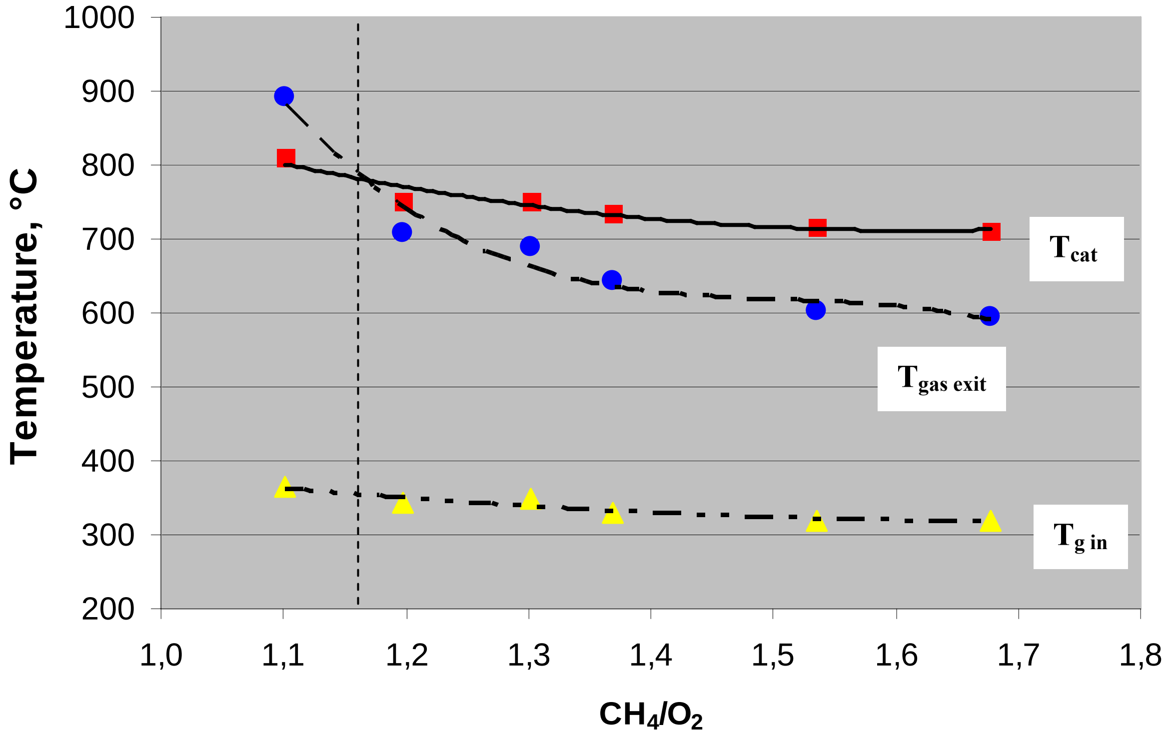


Figure 9 Effect of CH_4/O_2 feed ratio on the operating temperatures of LMR catalyst and downstream gas during high pressure fuel rich experiments.

Regarding the results of the analysis, table 4 reports a summary of the concentrations measured for the main species in the product stream together with the corresponding experimental conditions.

	Inlet Feed								
Run #	Power kW	CH4/O2	O2/CH4	CH4 g/s	Air g/s	Qt mol/s	P Bar abs	Preheat °C	CH4 %
_1	20,0	1,677	0,596	0,399	2,050	0,096	5,2	320	25,95
_2	20,0	1,5349	0,652	0,399	2,240	0,103	5,2	320	24,29
_3	20,0	1,3698	0,730	0,399	2,510	0,112	5,2	330	22,26
_4	20,0	1,3023	0,768	0,399	2,640	0,116	5,3	349	21,39
_5	20,0	1,1979	0,835	0,399	2,870	0,124	5,2	343	20,02
_6	20,0	1,1020	0,907	0,399	3,120	0,133	5,2	365	18,72
_7	20,0	1,7452	0,573	0,399	1,970	0,093	5,2	342	26,73
_8	20,0	2,0964	0,477	0,399	1,640	0,082	5,2	330	30,47

FEED			
CH4	O2 mmol/s	N2	Total
24,92	14,86	56,23	96,01
24,92	16,24	61,45	102,60
24,92	18,19	68,85	111,96
24,92	19,13	72,42	116,47
24,92	20,80	78,73	124,45
24,92	22,61	85,58	133,12
24,92	14,28	54,04	93,24
24,92	11,89	44,99	81,79

	Temperatures			Analysis					
Run #	Tg in	Tcat °C	Tg exit	H2	CO	CO2 % vol	CH4	O2	NOx ppm
_1	320	710	595	24,80	8,70	2,02		0,40	0,00
_2	320	717	603	27,3	9,9	0,91		0,4	0
_3	330	735	642	29,6	12,2	1,77		0,4	0
_4	349	751	688	29,2	11,2	1,75		0,45	0
_5	343	752	709	29,5	12,1	1,69		0,65	0
_6	365	811	893	31,4	13,3	1,6		0,3	0
_7	342	730	665	30,5	12,4	1,64		0,85	0
_8	330	692	609	28,7	10,3	1,72		0,8	0

Table 4 Summary of inlet conditions and main analysis results of fuel rich high pressure catalytic combustion tests. Run numbers correspond to conditions highlightened in figure 8.

Recommendation list for further test facility upgrading

The 3-week period spent by Dr. Stefano Cimino was intended to setup the high pressure catalytic reactor test rig after necessary modifications and upgrading eventually necessary to cope with fuel rich/catalytic partial oxidation approach and to start the experimental campaign. Unfortunately some delay was accumulated mainly due to the need to re-assemble, fix (some instrumentation failure occurred) and test the experimental rig after it was moved from a different location some months ago and. Moreover the experimental facility was originally designed and developed for high pressure catalytic combustion under ultra lean conditions. Has already pointed out such circumstance has important drawbacks when planning to operate under fuel rich conditions, which need to be addressed in order to operate under safe conditions and to obtain reliable data from a further experimental research activity.

One set of preliminary test run under fuel rich conditions was successfully performed during the visiting period. The data collected and the experience gained on the existing research infrastructure were used to prepare the following recommendation list which contains the main guidlines suggested to complete the upgrading the catalytic combustion experimental facility at KTH:

1. **Feeding Section and Combustor**

- Air Feed Line: substitute pneumatic valve control with Mass Flow Controller (max flow rate 60-80 kg/h). MFC should be preferably connected in line with the existing mass flow measurement device for calibration purpose.

  With actual configuration it is not really possible to effectively control the flow of air required (too low for the valve), thus affecting reliability of experimental data and also safety of operation (possible formation of explosive mix due to poor flow control.
- Modification of data acquisition & control software in order to have independent control of at least on 3 MFC (Air, Fuel, Inert).
- Fuel feed line: always use 2 gas cylinders connected together (connector is now available) to ensure safe fuel-rich operation (in order to avoid running out of fuel)
- Heating device for pressure gas regulator and pipes on fuel line. Multistage pressure reduction. Verification of the possibility for fuel gas preheating, possibly through injection at different location.
- Revaluate effectiveness of fuel feeding (and mixing) section inside the reactor through the venturi when system is operated with a reduced air-flow as in the case rich catalytic combustion.

2. **Analysis**

Typical product gas from the catalytic section of a rich catalytic combustor or a catalytic partial oxidation reactor operated with air include: H_2, CO, CO_2, CH_4, N_2, O_2.

At the moment the analysis is supposed to be carried out by a THC analyser for methane using a flame ionization detector with an hydrogen flame. In fact it was verified that the presence of H2 as a product in the mixture alters significantly the response of the FIDetector making impossible to measure unconverted CH_4 *or other Hydrocarbons.*

Regarding H2 measurement, the continuous analyzer available uses a thermal conductivity detector, which is not specific for H_2*, and therefore is strongly affected by the presence of other species different from nitrogen. The analyzer offer the possibility to correct the measure through a cross sensitivity method but this is only limited to the effect of CO which is measured at the same time (but not for* CO_2*,* CH_4*,* O_2 *which also affect the measure). Moreover cross sensitivity calibration would require independent calibration of H2 channel with a span gas containing only H2 and N2, presently not available.*

Two main possibilities might be considered (as alternatives or even in conjunction):

- A single continuous analyzer with 3 independent ND-IR devices for measuring CH_4 (0-20% vol) CO (0-20%vol) CO_2 (0-10%) and 1 TC detector for H_2 (max range 0-40% vol.) with automatic correction for the interference of the other 3 measured species. A calibration mixture of H_2 in N_2 is required apart from normal spag gas mix for the other 3 species. This solution has the advantage of real time analysis of all the major species (including reliable H2 measure through complete and automated cross sensitivity routine), whereas no internal standard can be used for mass balance calculation. Oxygen may be measured by existing paramagnetic analyser.

- Gas chromatography, better micro GC, specifically set-up for the measurement of permanent gases and H_2. In this case it would be important and useful to measure also the N2 concentration in order to use it a san internal standard. Typical product gas vol. conc.: H_2=10-30 %, CO=5=15; CO_2=0,5-5%; CH_4=0,1-10%; N_2=30-60%, O_2=0.01-1%. A single calibration mixture with all the species within the selected range can be used. Main advantage: complete measurement of all species conc.. Drawbacks: analysis time from 1-2 min. with microGC to 15-20 with normal GC; system has to be optimized for this specific analysis and may require different carrier gases (He and Ar).

In both cases water has to be removed from the gas mix sampled from the reactor since its presence affects the measurement.

3. Control & Data acquisition software

As already pointed out, the main modifications to the hardware of the experimental rig must be followed up by an upgrading of the control and data acquisition software, with special regard to:

1. Independent control and measure of MFC with the possibility to set characteristic parameters for specific gas
2. Flexibility in setting of safety guard parameters, not anymore connected to the operation limited under fuel lean conditions.
3. Acquisition of signals from new analyser (continuous). In the case gas chromatographic analysis a separate PC will be needed to operate and control the instrument.

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