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Catalytic combustion concept for gas turbines

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Abstract

Catalytic combustion for gas turbines was investigated, based on a partial catalytic combustion section followed by a homogeneous combustion zone. A pressurized test rig (<25 bar) was built to test the influence of various parameters on this concept using Pd and Pt catalysts.

The pressure influence on the apparent catalytic reaction rate was of the order 0.4, assuming that the reaction kinetics could be described by a power rate function which was of first order with respect to methane. Pd catalysts showed a pressure-dependent temperature for the transition of the active PdO to the much less active Pd. Combining Pd and Pt within one catalyst resulted in a considerably lower transition temperature.

Homogeneous combustion reactions set on from 650°C, depending on the methane concentration, pressure and flow. With inlet temperatures above 800°C the homogeneous combustion always started. At outlet temperatures below 1050°C high CO concentrations could be measured. At higher temperatures the CO, CH_4 and NO_x concentrations were lower than 5 ppm. During several experiments total conversion of CH_4 and CO was observed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic combustion; Gas turbine; Palladium combustion catalysts; Platinum combustion catalysts; Palladium–platinum combustion catalysts; Sulphur poisoning

1. Introduction

Catalytic combustion is seen as one of the promising techniques to reduce the emissions of NO_x for gas turbines, while keeping the CO and unburnt hydrocarbons emissions also low. Conventional NO_x emissions reducing techniques as lean combustion have the disadvantage that at reduced power the emissions of CO and C_nH_m can increase significantly. Catalytic combustion is believed to be much more stable at reduced power, resulting in a greater turn-down ratio with low emissions.

The combustion concept is based on a catalytic combustion zone followed by a homogeneous combustion zone (“liner”). The reason for this hybrid concept is that at elevated pressures the homogeneous combustion reactions will start at reasonably low temperatures (800–900°C) and complete the combustion. An ultra-high temperature catalyst is therefore not needed.

Developing such a catalytic combustion system for gas turbines is one of the goals of Brite-Euram project 5846 “Catalytic Combustion system Concepts for Pollutant Suppression in Industrial Gas Turbines, Reformers and Radiant Heaters”. As part of this project a pressurized test rig (<25 bar) was built, where the concept of partial catalytic and homogeneous combustion was tested at simulated gas turbine conditions.

To develop and test this concept the following points are of interest:

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- The catalytic activity related to the inlet temperature. The inlet temperature depends on ambient temperature, power output, pressure and compressor efficiency. Typically the compressor outlet temperature varies from 360°C to 400°C as the shaft power goes from 40% to 100%.
- The influence of the different process parameters, such as pressure, temperature, methane concentration, etc., on the activity of the catalysts.
- The combustion rate in the homogeneous section related to the temperature and the reaction time (liner length). Of course this temperature is influenced by reactant concentrations, flow and pressure.
- The performance of several catalysts supplied within the scope of this Brite Euram project.

Experiments were carried out to examine these points of interest. The aim is to prove whether the concept of catalytic combustion followed by homogeneous combustion is useful for industrial gas turbines. The results of these experiments will be given and discussed in this paper.

2. Experimental

In Fig. 1 an overall scheme of the test rig is given. Experiments were carried out at pressures up to 21 bar and gas outlet temperatures up to 1100°C. The air flow rate varied between 30 and 145 $m^3 h^{-1}$ (1.013 bar, 0°C).

Ambient air was compressed in two stages to 30 bar and the resulting flow was passed through a plenum and pressure regulator. In the electrical heater (42 kW) the air was heated to the desired inlet temperature (<650°C). Natural gas or pure methane was injected just in front of a static mixer. The reactor part consisted out of one or two catalysts and an empty tube (homogeneous combustion section). The flow through the test rig was regulated with the outlet valve.

A detailed scheme of the reaction part is given in Fig. 2. The catalysts were attached with ceramic cement to the inlet pieces in order to avoid leakage around them. The catalysts and all inner casings were well insulated to ensure adiabatic behaviour. All inner parts of the reaction section (catalyst holders, inlet pieces and liner) consisted of a special heat-resistant steel (Thermax nr 14762).

Gas temperatures were measured by K-type thermocouples (0.5 mm) just before and behind the catalysts and at several distances in the homogeneous section. Catalyst temperatures at several distances along the axis were measured by placing thermocouples in catalyst channels. These channels were blocked by ceramic cement in order to ensure proper temperature measurement.

Gas samples were taken upstream and downstream of the catalyst, at different distances in the liner and after the cooler. The composition of the samples was measured on line. CO_2, CO and CH_4 concentrations were determined with NDIR analysis (MAIHAK 600). NO_x was analysed by chemiluminescence (Eco Physics CLD 700 EL-ht) and O_2 by paramagnetism

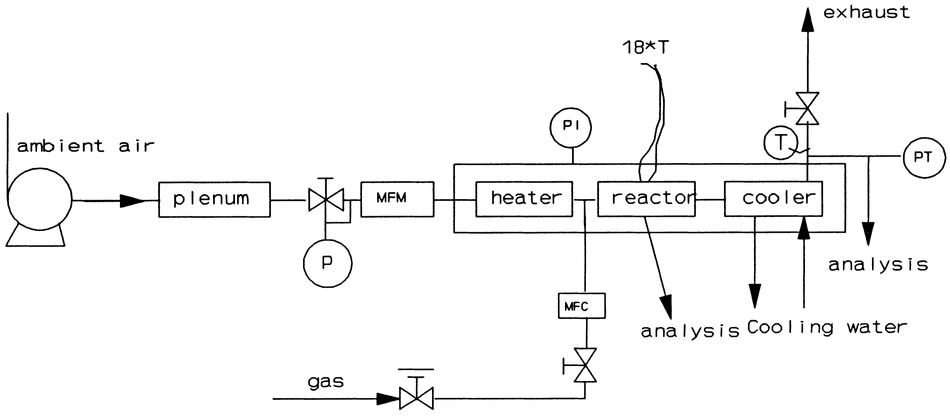

Fig. 1. The test rig.

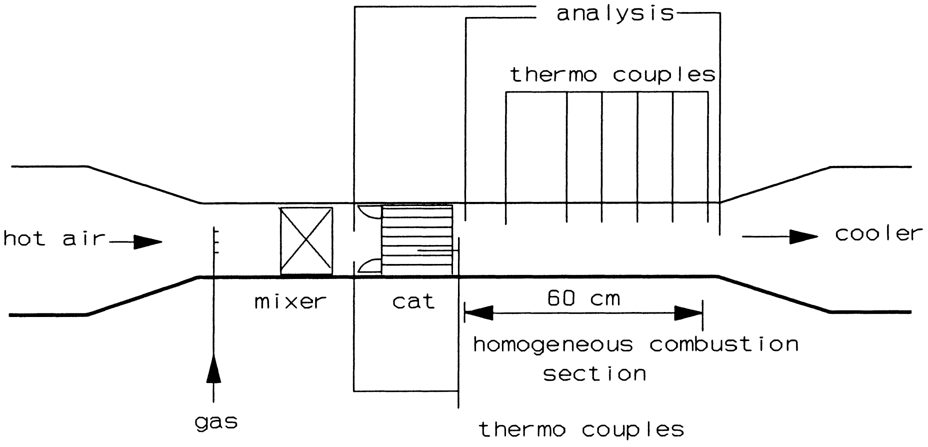

Fig. 2. The reaction section with one catalyst.

(MAIHAK OXOR 610). Switching valves were used to obtain samples from different points. The gas samples were taken with uncooled stainless steel (316) tubes with an inner diameter of 0.7 mm. The pressure drop in these small diameter tubes results in a quick quench of the reactions in the tubes. Before analysis water was removed from the samples by a chiller.

Air and gas flow were measured by mass flow controllers. Calculated methane concentrations based on the measured flows did not differ more than 5% from the measured concentrations upstream of the catalysts. Calculated conversions based on temperature rise of the gas stream over the catalysts and based on the gas analysis did not differ by more than 5%. In cases where homogeneous combustion took place, the difference over the homogeneous combustion zone could be 15%. The high temperatures (up to 1100°C) of the liner would increase the heat leakage to the outer wall.

2.1. Catalysts

All catalysts were prepared by Degussa AG, Germany. Pd- and Pt/Pd-based catalysts were tested as first and second catalysts. A Pt-based catalyst was also tested as a second catalyst.

The catalysts were applied into corderite honeycombs with square channels. The corderite was covered with a washcoat on which the active metal was dispersed. The catalysts differed in kind of washcoat, washcoat loading, metal loading and cell density. In Table 1 the properties of the different catalysts are given.

Table 1
Characteristics of the catalysts tested in this study

Catalyst	Active component	cpsi	Open frontal area (%)	Channel diameter (mm)
VST-301	Pd	200	62	1.6
VST-302	Pt/Pd	400	74	1.23
VST-303	Pt/Pd	200	62	1.6
VST-304	Pd	400	74	1.23
VST-305	Pd	100	56	2.14
VST-306	Pd	400	74	1.23
VST-307	Pd	400	74	1.23
VST-328	Pt	400	74	1.23

2.2. Catalytic activity

Catalytic combustion is a complicated process, in which several transport and reaction mechanisms are involved. First methane and oxygen are transported from the gas stream to the porous surface of the catalyst. Then, these components have to diffuse into the pores and adsorb at the surface. After reaction at the active sites the products desorb and are transferred to the gas stream again by pore diffusion and external mass transfer. If the catalyst is very active, then mass transfer of the reactants to the surface is the limiting mechanism in the process. On the other hand, if the reaction is very slow, then the reaction kinetics are rate-determining. The reaction rate is dependent on the temperature and due to the temperature rise over the catalyst by increasing conversion the overall rate can first be controlled by the kinetics and at the end of the catalyst by mass transfer.

In order to make a proper comparison between the various catalysts, a simple model was used to be able to estimate the catalyst activity. In this model a correction for the catalyst surface area and external mass transfer resistance on the conversion was made.

The model is based on the following assumptions:

- no radiation,
- no end losses of heat at the inlet and outlet of the catalyst,
- no axial heat conduction in gas and solid phase,
- no homogeneous combustion in the channels,
- the catalytic reaction kinetics are first order with respect to methane, and
- temperature difference over the washcoat is negligible.

If the reaction rate is very low as compared to the mass transfer, then the total surface area of the pores inside the washcoat is used. However, if the reaction rate becomes higher, then a part or even only the external surface of the washcoat is used. The part of the washcoat which is used is defined by the effectiveness factor, which is difficult to calculate because many of the physical properties of the washcoat need to be known. To overcome this problem an apparent reaction kinetics is defined, which incorporates the effectiveness factor.

In steady state the process can be described by the following equation:

$$J_z\,\mathrm{d}z = kg(\mathrm{CH}_{4_\mathrm{b}} - \mathrm{CH}_{4_\mathrm{i}})\,\mathrm{d}z = k_{00_\mathrm{app}} \times \exp(-E_{\mathrm{a}_\mathrm{app}}/RT_z)\mathrm{CH}_{4_{\mathrm{i},z}}$$

$$\mathrm{d}z = \frac{F(\mathrm{CH}_{4_z} - \mathrm{CH}_{4_{z+\mathrm{d}z}})}{\pi d_k}. \qquad (1)$$

The model further assumes that all the heat is generated at the surface and transferred by forced convection to the gas/air stream:

$$Q_z\,\mathrm{d}z = \alpha(T_\mathrm{cat}(z) - T_\mathrm{g}(z))\,\mathrm{d}z. \qquad (2)$$

The heat transfer coefficient can be calculated by the following equation [1]:

$$Nu = 0.0214(Re^{0.8} - 100)Pr^{0.4}(1 + d_\mathrm{c}/l^{2/3}),$$
$$2300 < Re < 1E6; \quad 0.5 < Pr < 1.5;\ d_\mathrm{c}/l < 1, \qquad (3)$$

which is valid for the experimental conditions in this study. From the experimental data a heat transfer coefficient could be calculated. Fig. 3 shows that the experimental and calculated Nusselt numbers compare rather well. The scatter at higher Reynolds numbers is caused by the inaccuracy of the calculations due to the small temperature rise over the catalyst.

The mass transfer coefficient (kg) can also be calculated by Eq. (3) using the Chilton–Colburn analogy. With kg the external mass transfer resistance and the CH_4 concentration at the washcoat surface can be calculated.

$E_{\mathrm{a}_\mathrm{app}}$ and k_{00_app} are found by measuring the catalyst temperature (T_s) and the conversion over the catalyst. The reaction rate is corrected for external mass transfer and an Arrhenius plot is constructed by plotting the reaction rate against the average catalyst temperature. The slope of the resulting line is $-E_{\mathrm{a}_\mathrm{app}}/R$ and the intercept at the y-axis yields k_{00_app}.

This method eliminates the effects of flow, pressure, number of channels, inlet temperature, etc. on the measured activity. Therefore it is possible to compare different catalysts with respect to activity.

3. Results

3.1. Apparent kinetics

For all catalysts "apparent" Arrhenius plots were made. Fig. 4 shows such a plot for two catalysts, clearly showing that the model yields reasonable results. In Table 2 the results (i.e. $E_{\mathrm{a}_\mathrm{app}}$ and k_{00_app}) for all the catalysts are presented.

3.2. Ignition temperatures

For all catalysts ignition temperatures were recorded. Deactivation of the catalyst turned out to increase the ignition temperature. Most of the catalysts yielded ignition between 320°C (fresh) and 400°C.

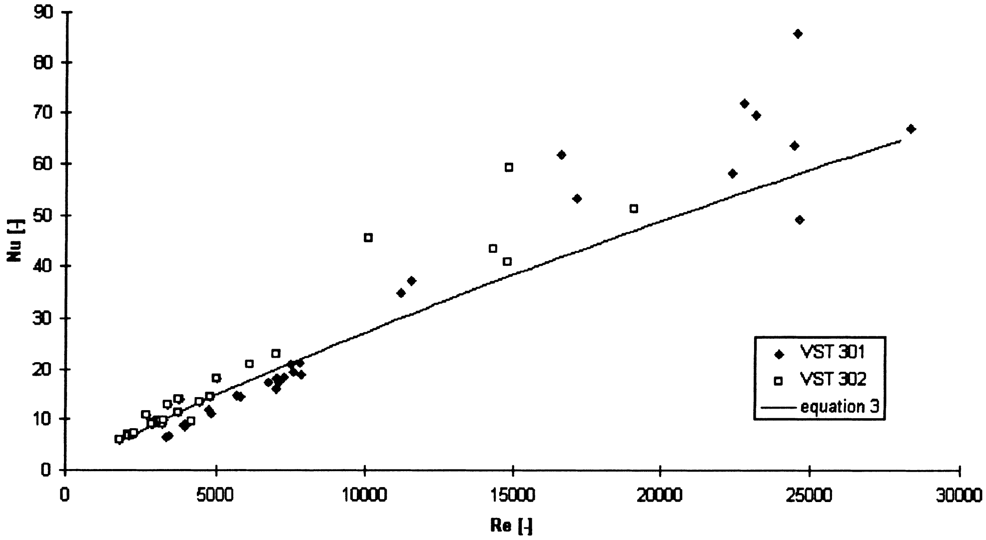

Fig. 3. Heat transfer in the catalyst: experimental and theoretical Nusselt numbers versus the Reynolds numbers.

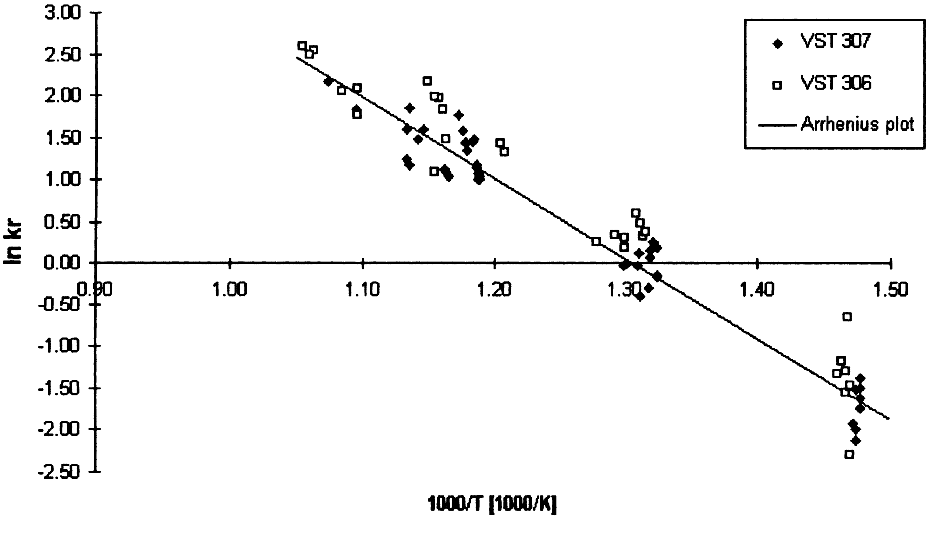

Fig. 4. Arrhenius plot of k_{app}.

3.3. Inlet temperature and concentration

First the influence of the different process parameters was measured. Fig. 5 shows that inlet temperature and methane concentration can have a considerable influence on the conversion. At some conditions just a small change in inlet temperature or concentration may initiate the reaction.

3.4. Pressure influence

Fig. 6 shows the influence of pressure on the conversion at a constant mass flow. The effect of pressure on the apparent kinetics was determined by using the model. For each experiment the value of $k_{r_{\mathrm{app}}}$ was determined and divided by $k_{r_{\mathrm{app}}}$ calculated from Table 2. This ratio is pressure

Table 2
Kinetic parameters for the tested catalysts

Catalyst	$E_{a_{app}}$ (kJ mol^{-1})	ln($k_{00_{app}}$) ln(mol m^{-2} s^{-1})
VST 301	35±6	7.5±0.9
VST 302	40±5	7.2±0.5
VST 304	60±5	9.7±0.9
VST 305	50±5	8.6±0.9
VST 306	80±5	12.6±0.8
VST 307	80±5	12.6±0.8
VST 328	150±20	19.0±2.6

dependent as can be seen in Fig. 7. The slope of the resulting line is the order in pressure yielding 0.4±0.1.

3.5. *Influence of gas velocity*

In a real aero-derived gas turbine the gas velocity at the combustor inlet can be about 30 m s^{-1}. However, the maximum velocity that could be reached in the experimental set-up was 11 m s^{-1}. To determine the effect of higher velocities the inlet diameter was reduced resulting in a maximum velocity >30 m s^{-1}. The results of these tests are shown in Fig. 8. It shows that these results are consistent and can be described by the model.

3.6. *PdO→Pd transition*

Farrauto et al. [2] showed that at a certain temperature PdO transforms into the catalytically less active Pd. This transition temperature is a function of the partial O_2 pressure. We also observed a pressure influence on the transition temperature for PdO catalysts. The transition temperature of the catalysts was determined experimentally by increasing the methane concentration or the inlet temperature. The transition temperature is clearly recognized as the point where increasing the methane concentration or inlet temperature had no influence on the catalyst temperature. In Fig. 9 the results of such an experiment are given.

Catalysts with Pt and Pd have also been investigated. Using Pt, which has no transition temperature and is used at higher temperatures, should increase the activity at temperatures above the transition temperatures. Instead of an increase in activity lower transition temperatures were found. The pressure dependency of the transition temperature for Pd and Pd/Pt is represented in Fig. 10 together with results of Griffin [3] and Dalla Betta et al. [4]. The line of Dalla Betta et al. [4] is based on one measurement at 11 bar and calculated for the other pressures. Fig. 10 shows that our results for Pd catalysts are in agreement with literature. Combining Pt and Pd within one catalyst is not useful, because of the lowering effect on the transition temperature.

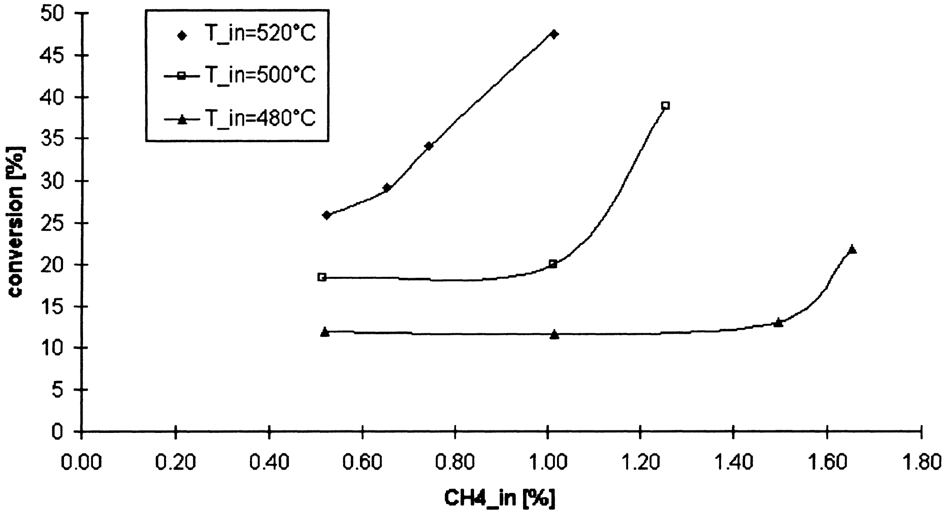

Fig. 5. The influence of CH_4-concentration and inlet temperature on conversion.

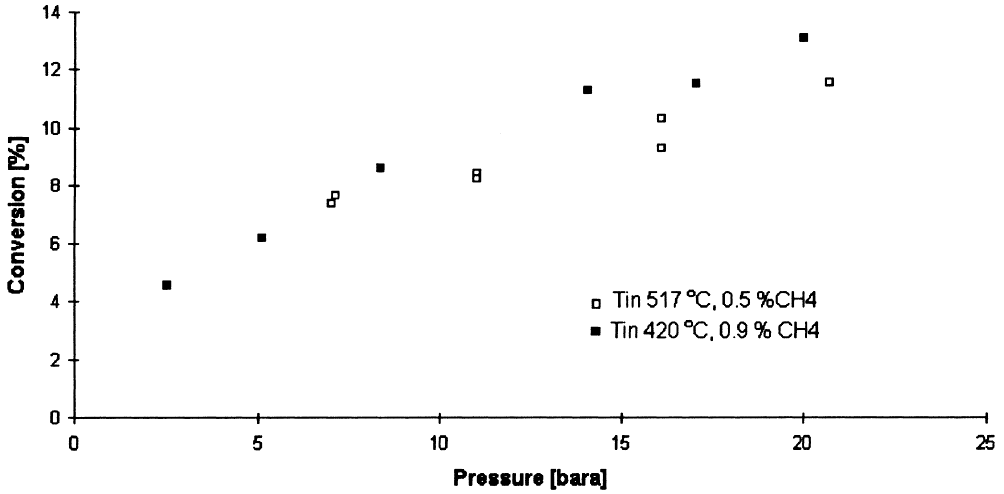

Fig. 6. The influence of pressure on conversion at constant mass flow.

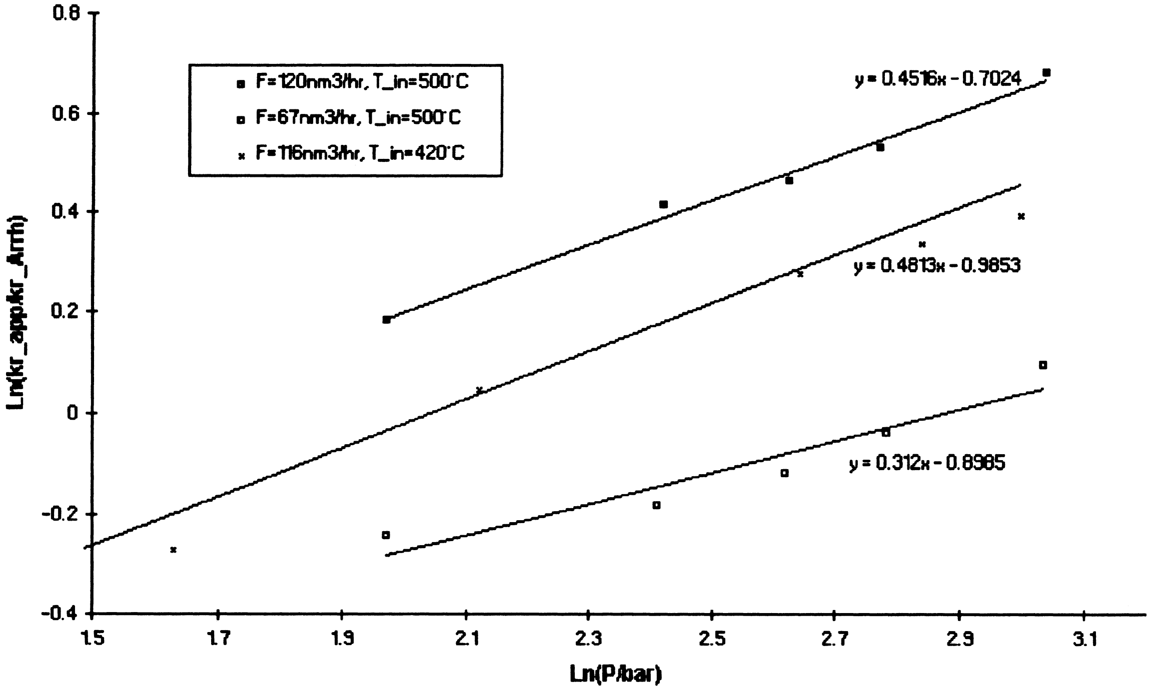

Fig. 7. The influence of pressure on the reaction rate.

3.7. *Second stage catalyst*

The idea behind the concept was to raise the temperature of the gas/air mixture to such a level that the homogeneous reactions would complete the combustion. This was tested with two Pd-based catalysts in series and with a combination of a Pd catalyst and a Pt catalyst. The conversion between the catalysts was determined from the measured gas temperature between the two catalysts.

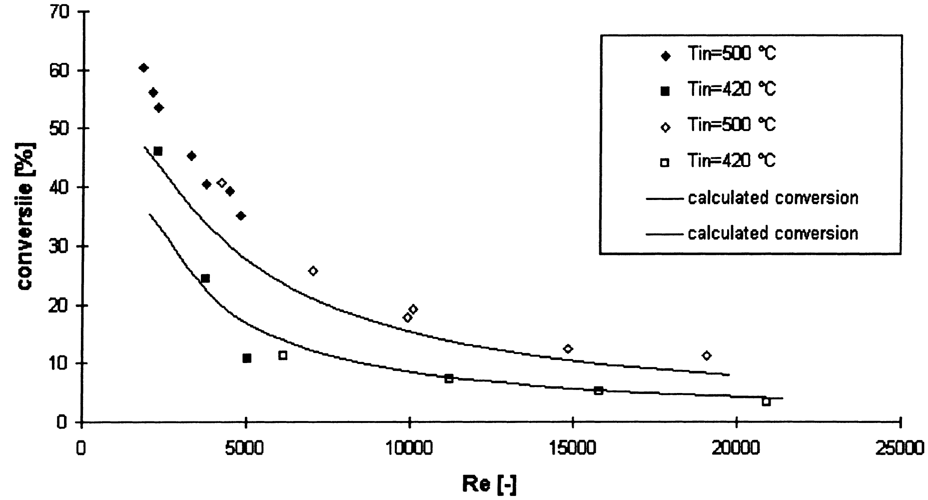

Fig. 8. The influence of the Reynolds number on conversion.

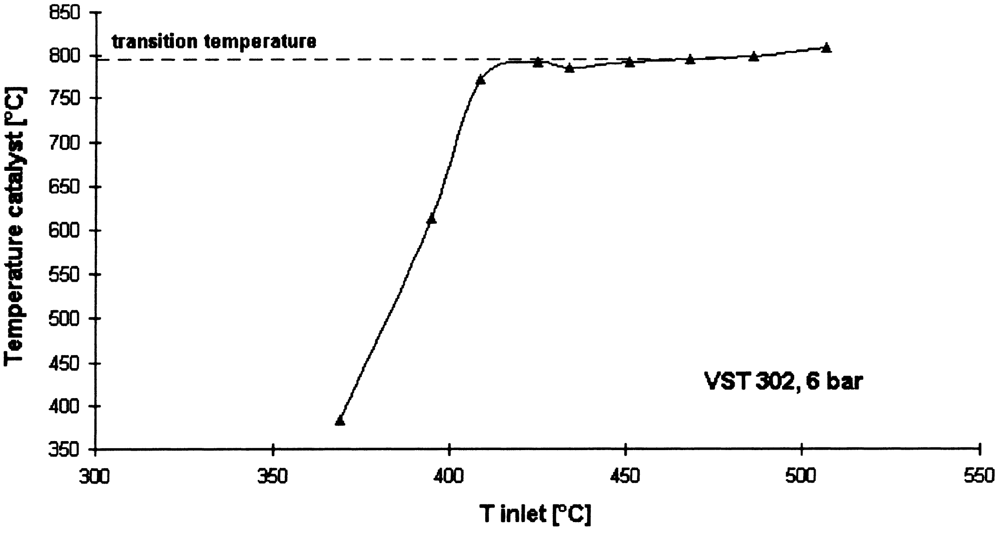

Fig. 9. The catalyst temperature as a function of inlet temperature.

In Fig. 11 the conversion over the Pt catalyst as a function of the inlet temperature is shown. This shows that under our conditions at least an inlet temperature of 650°C is necessary to initiate the catalytic reactions within the Pt catalyst. At these temperatures homogeneous combustion is also possible. However, homogeneous combustion was not observed in our experiments, since the wall temperatures of the catalysts were considerably higher than the gas temperatures.

3.8. *Homogeneous combustion*

Homogeneous combustion is very important for the concept. The catalysts are used to increase the temperature to such a level that the homogeneous reac-

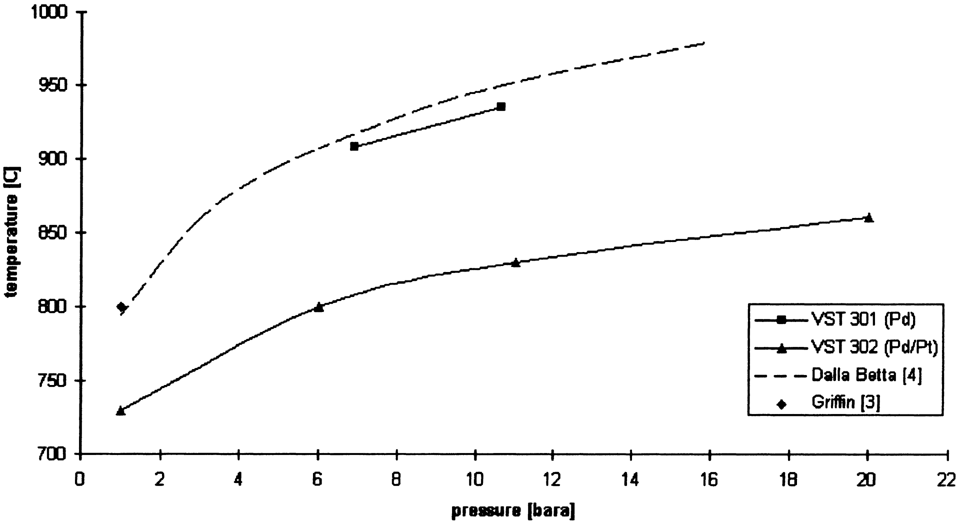

Fig. 10. The influence of pressure on the PdO/Pd transistion temperature.

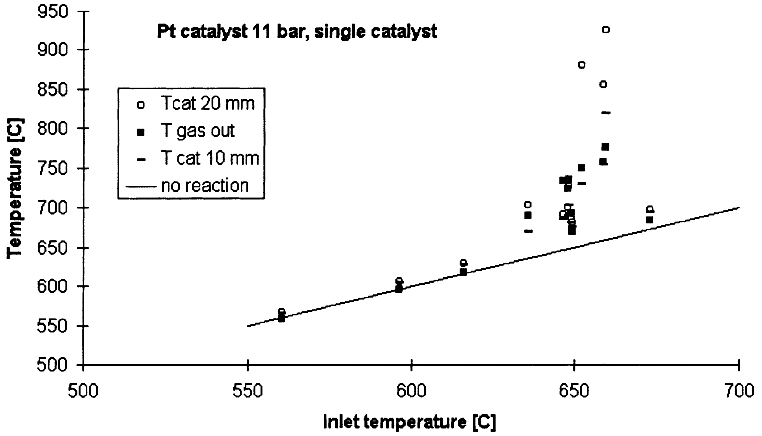

Fig. 11. The activity of a Pt catalyst.

tions will complete the combustion. During the experiments the gas was analysed just behind the catalysts and at some points along the axis of the liner and after the cooler. It turned out that using these catalysts no CO was produced.

As mentioned by Vortmeyer [5] large amounts of CO were found when the liner outlet temperatures lie in the range 650–1050°C. At higher outlet temperatures no CO was detected (see Fig. 12). In this figure also some results for measurements in the liner are given. Checking these results with the calculated conversion based on the temperature rise gave a good comparison. This indicated that the reaction was quenched quickly in the sampling tubes.

The outlet temperature of the homogeneous combustion zone as a function of the inlet temperature is given in Fig. 13 for several experiments at 11 and 20 bar. This figure shows clearly that the inlet temperature is an important parameter. However, we also observed that homogeneous combustion was influenced by other parameters, such as methane concentration and residence time in the liner. The results in this figure are similar to those of Hayashi et al. [6] and show that 650°C is the minimum temperature to

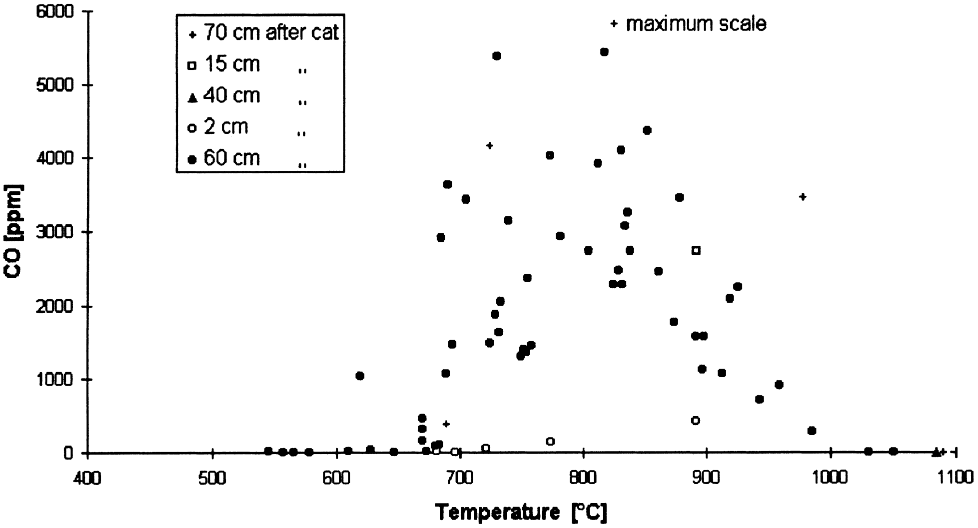

Fig. 12. CO production in the homogeneous combustion zone.

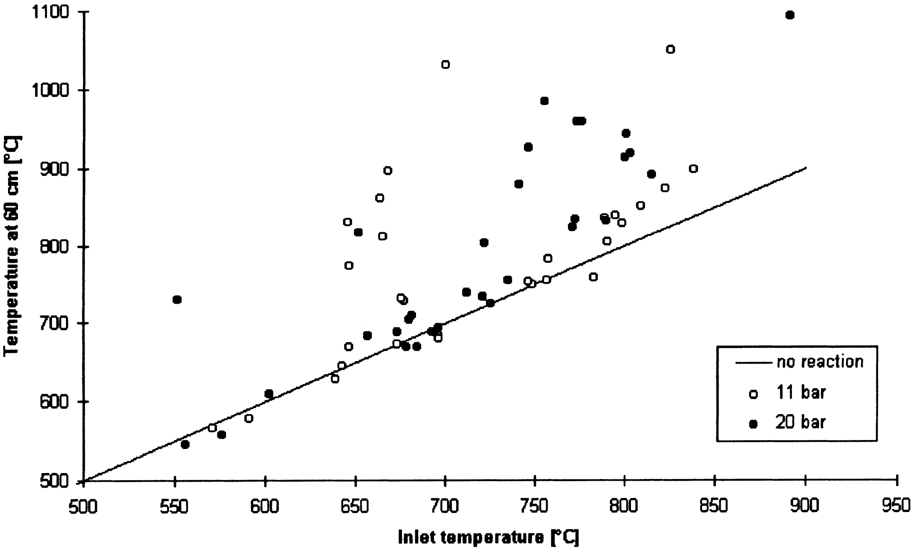

Fig. 13. The outlet temperature of the homogenous combustion zone as a function of the inlet temperature.

initiate homogeneous combustion. Above 800°C homogeneous combustion will most certainly take place.

In aero-derivative gas turbines the gas/air flows are much higher yielding a shorter residence time. The necessary outlet temperature of the last catalyst should therefore be much higher than 800°C.

3.9. *Total concept*

Due to material limitations of the test rig the maximum allowable gas outlet temperature was 1100°C. Proving the total concept would be reaching 100% conversion of CH_4 with a modest inlet temperature for the first catalyst and having low CO, CH_4 and NO_x

Table 3
Experiments with total conversion of methane

Cat 1	Cat 2	P (bar)	T_{in} (°C)	Flow ($m^3 h^{-1}$)	CH_4 (vol%)	T_{out} (°C)	$CH_{4_{out}}$ (ppm)	CO_{out} (ppm)	T_{ad} (°C)	ad (%)
302	Inert	11.8	460	68	2.7	1050	3	4	1216	78
302	Inert	11.3	500	102	2.7	1054	0	0	1256	73
302	Inert	20	450	129	2.2	960	0	4	1066	83
302	Inert	20.4	500	108	2.2	953	0	0	1116	74
302	302	20	434	115	2.3	943	0	713	1078	79
302	–	20	400	108	2.3	959	0	903	1044	87
301	–	20	525	103	2.5	1090	0	0	1225	81

emissions. The emissions of NO_x are expected to be low at these outlet temperatures and turned out to be below the detection limit of 1 ppm. During several experiments complete combustion was reached, with low NO_x, CH_4 and CO emissions. In Table 3the results of these experiments are presented.

Also the adiabatic behaviour of the total reaction section (catalyst and homogeneous combustion zone) is given in Table 3. The total adiabatic behaviour is around 80% (ratio calculated heat uptake in flue gas based on measured temperatures divided by the calculation based on measured concentrations). In the catalytic section 5% of its heat input was lost, while in the homogeneous combustion zone 15% was lost due to the high temperature difference between the steel tube and its surroundings.

4. Discussion

The aim of this study is to compare different catalysts at gas turbine conditions and to prove whether the concept of partial catalytic combustion followed by homogeneous combustion is useful. The experimental gas flow was relatively low, but the results can be translated to real gas turbine conditions.

In this study long-term stability and activity of the catalysts were not investigated. The catalysts were fresh and some initial deactivation was observed. However, as Furuya et al. [7] mentioned, some not understood deactivation and reactivation of Pd catalysts was also found. Also deactivation was found after the catalysts had been exposed to the PdO/Pd transition temperature or even higher temperatures due to oscillations inside the catalyst or in the homogeneous combustion zone.

The water content of the combustion air was very low due to the compression and drying of the combustion air. In normal gas turbines the water content will be much higher, especially when a pre-burner is used to increase the inlet temperature. Water content can have a considerable influence on the activity of the catalyst according to van Giezen et al. [8]. This effect should therefore be determined under real conditions.

In our experiments odourized natural gas was used. Due to odourization some sulphur is present in the gas. Sulphur is also known to deactivate Pd catalysts. A small test was done using pure methane instead of natural gas. During this test no difference in activity was observed.

The gas temperature at which the homogeneous reactions will start and complete the combustion within the given residence time is very important for this concept. This gas temperature is related to the catalyst temperature and by the heat transfer between gas and catalyst wall. In our experiments the catalyst temperature was 100–150°C higher than the gas temperature. For instance a gas temperature of 900°C results in a catalyst temperature of about 1000–1100°C, which is too high for Pd catalysts. A lower gas temperature for homogeneous combustion is possible if the residence time for homogenous combustion increases. Gas turbines which have enough combustor space can therefore probably be equipped with only Pd catalysts. Aero-derivative gas turbines have very low residence times and therefore need a combination of a Pd catalyst and a high-temperature catalyst like, for instance, a Pt catalyst.

The total concept could be proved for the case of 40–100% power. However, for gas turbine application a pre-burner is probably necessary to start the system and to be able to increase the inlet temperature of the first catalyst at lower power. Using a pre-burner also gives more freedom of operation, thus increasing the possibilities for process control. Unfortunately the NO_x emission would increase.

5. Conclusions

1. Pressure has an influence on the reaction kinetics. Assuming the reaction kinetics can be described by a power rate law the order with respect to the pressure is 0.4. The reaction kinetic can be written as follows: $r = k_{00_{\mathrm{app}}} \exp(E_{a_{\mathrm{app}}}/RT)[\mathrm{CH_4}][P/P_0]^{0.4}$.
2. Palladium can be used as the only catalyst depending on the required gas outlet temperature of the last catalyst. Gas turbines with very short residence times (aero derivatives) probably need a combination of Pd and a catalyst which can withstand higher temperatures.
3. Using Platinum on a Palladium catalyst does not increase the activity at temperatures above the transition temperature of PdO→Pd. Even a considerable lowering of the transition temperature was found.
4. Homogeneous combustion was observed at temperatures above 650°C depending on the CH_4 concentration, total pressure and mass flow.
5. At gas outlet temperatures above 1050°C no CO and CH_4 were found.
6. The concept of partial catalytic and partial homogeneous combustion is capable to yield low NO_x as well as low CO and CH_4 emissions. However, to start up and to control the system a pre-burner is probably necessary.

6. Notations

A_{int}	internal surface (m^2)
d	channel diameter (m)
CH_4	methane (vol%)
E_a	activation energy (kJ mol^{-1})
F	flow rate at normal conditions (1.013 bar, 0°C) ($m^3\ h^{-1}$)
ΔH	combustion enthalpy (kJ mol^{-1})
J	mole flux (mol m^{-2})
kg	mass transfer coefficient (m s^{-1})
k_{app}	apparent rate of reaction (mol $m^{-2}\ s^{-1}$)
$k_{00_{\mathrm{app}}}$	preexponential factor in reaction rate
k_1	rate of reaction (mol $m^{-2}\ s^{-1}$)
l	length (m)
Nu	Nusselt (dimensionless)
Pr	Prandtl (dimensionless)
Q	heat flux (J m^{-2})
Sc	Schmidt (dimensionless)
Sh	Sherwood (dimensionless)
R	gas constant (J $mol^{-1}\ K^{-1}$)
Re	Reynolds (dimensionless)
T	temperature (K)

Greek letters

α	heat transfer coefficient (W $m^{-2}\ K^{-1}$)
η	effectiveness factor k_{app}/k_1 (dimensionless)
ρ	density (kg m^{-3})

Indices

b	bulk
c	channel
cat	catalyst
g	gas
i	interface
z	axial coordinate

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