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Catalytic combustion of low heating value gas mixtures: comparison between laboratory and pilot scale tests

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Abstract

Catalytic combustion of low heating value fuels is a promising method for electricity production combining the use of a renewable fuel with ultra-low emissions. In the present work, catalytic combustion of a low heating value gas has been studied over monolithic catalysts in an atmospheric 30 kW pilot catalytic combustor connected to a wood pellet gasifier. The results have been compared to similar tests with a model gas mixture and a series of test in a laboratory scale reactor for monolithic samples. Various catalyst configurations have been tested, such as precious metal-based catalyst impregnated on modified alumina washcoats and hexaaluminate washcoats. Cordierite monoliths with various cells per square inch were used as supports, but hexaaluminate extruded monoliths were also used. The catalysts were combined in different segment series.

The results show that it is possible to ignite the low heating value gas at compressor outlet temperatures without the use of pre-burners over precious metal catalysts. Generally, trends and phenomena obtained in laboratory reactor operating close to isothermal could be confirmed in the pilot operating at close to adiabatic conditions. Further results, such as deactivation by sulphur compounds, fuel-NO_x conversion and emissions of carbon monoxide and total hydrocarbons, are addressed in the paper. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic combustion; NO_x conversion; NO_x emission; Low heating value fuels

1. Introduction

High temperature catalytic combustion is a promising new technology. For gas turbine applications it is considered to be one of the most promising and cost effective techniques for reducing NO_x emissions [1] and for natural gas fired turbines with catalytic combustors single digit values have been achieved, i.e. <10 ppm of NO_x [2]. During the last decade most of the interest has been focused on catalytic combustion of natural gas, but other fuels are also of interest. One example is the use of low heating value (LHV) fuels. As a result of the growing concern for the effects of increasing emissions of CO_2, caused by the extensive use of fossil fuels, the use of biomass for power production has increased. One of the most efficient ways of converting the energy content of the biomass into electricity is by using the integrated gasification combined cycle (IGCC) concept. The gas produced from biomass gasification will have a lower heating value of around 5 MJ/m_n^3 and typical concentrations of the main components for such a gas are shown in Table 1. Apart from the main gas components there are also significant amounts of trace gases that play a significant role, e.g. ammonia, hydrogen cyanide and hydrogen sulphide [3]. Due to the gas quality require-

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Table 1
Gas from gasification of wood and synthetic model gas mixture resembling the composition of the gasified biomass

	CO (vol.%)	CO_2 (vol.%)	H_2 (vol.%)	H_2O (vol.%)	N_2 (vol.%)	CH_4 (vol.%)	C_2H_4 (vol.%)	LHV (MJ/m_n^3)
Gasification gas	15.4	11.8	12.6	10.0	47.1	2.6	0.4	4.5
Synthetic model gas	14.7	13.8	9.9	11.2	44.8	4.6	1.0	5.1

ments put by the gas turbine there are very strict limits on certain trace compounds, especially chloride, alkali metals and particles, resulting in a demand for efficient gas cleaning prior to combustion [4]. On other components, such as ammonia and hydrogen cyanide, there are no technical limitations but these can on the other hand contribute to the formation of large quantities of fuel-NO_x. With respect to the special restrictions and demands of this fuel, such as low heating value, high levels of hydrogen and carbon monoxide and potentially high levels of fuel-NO_x, catalytic combustion could be an attractive solution in gas turbines. Since the formation of thermal NO_x in the combustion of such an LHV-gas is very low, the effect of the catalyst will have on the conversion of fuel nitrogen to NO_x is of special interest. For conventional flame combustion of this kind of LHV-gas the amount of ammonia converted to NO_x is a function of both the combustor design and the total ammonia concentration with values in the range between 30 and 70% reported in [5,6]. However, low conversions of ammonia to NO_x, i.e. down to 30%, are usually only achieved at high total inlet concentrations of ammonia. Hence, the overall outlet concentration of NO_x is still high. Laboratory studies have shown that the catalyst has a strong effect on the nitrogen chemistry [7] and that catalytic combustion has a potential to reach lower values than flame combustion, especially at low inlet concentrations of ammonia, but this has not previously been studied on a larger scale.

Within the ULECAT project, a project within the framework of the European research programme JOULE, the potential to use catalytic combustion for such an application have been investigated. The general objective of that project was to develop an ultra-low emissions gas turbine in the range 1–5 MWe, able to run with both biomass-derived gases and liquid fuels [8]. The target values of the project were

- thermal efficiency of the gas turbine >35%,
- UHC <25 ppm (15% O_2),
- CO <50 ppm (15% O_2),
- NO_x <25 ppm (15% O_2),
- fixed nitrogen conversion <10%.

In this presentation, experiments performed in a catalytic combustion pilot test rig, using both biogas produced in an atmospheric air blown gasifier and a synthetic model gas mixture resembling such a gas, are described. The objective of the present paper is to describe the pilot scale test facility and to compare the results reported here from this unit with results from previous laboratory scale tests. The main difference between the pilot and the laboratory scale experiments is that the former is performed under close to adiabatic conditions and that the latter is performed close to isothermal conditions. The effect of low concentrations of sulphur is one of the differences between the model gas experiments, which are based on a sulphur free gas, and the gas produced from gasification, which contains low amounts of sulphur compounds. It has previously been shown in laboratory scale experiments that even low concentrations of hydrogen sulphide or sulphur dioxide significantly influence the catalyst activity [3]. It should also be remembered that both the pilot and the laboratory scale experiments are performed at atmospheric pressure while the combustion in the aimed application always is performed at elevated pressure. The problems connected with pilot scale testing at atmospheric pressure and scale-up to gas turbine operation at full-scale and pressure have previously been addressed, e.g. by Kolaczkowski [9] and Groppi et al. [10].

1.1. Background to hexaaluminate-based catalysts

This study has mainly focused on hexaaluminate-based catalysts, e.g. manganese-substituted lanthanum hexaaluminate or palladium or platinum impregnated lanthanum hexaaluminates. It has been shown previously, that one of the most promising groups of high temperature stable combustion catalysts is hexaaluminates [11–14]. The hexaaluminate structure has the general formula $AB_xAl_{12-x}O_{19-\alpha}$, where the A ion could be an alkali, alkaline-earth-metal or rare-earth-metal. Some of the aluminium ions can be substituted by transition metal ions with similar radii and charge. It has been shown that the choice of both A and B ions can effect the catalytic activity and the thermal stability of the resulting substituted hexaaluminate. In previous papers, various hexaaluminates have been prepared. It was shown that hexaaluminates, e.g. $LaMnAl_{11}O_{19}$ and $LaAl_{11}O_{18}$, could be prepared with surface areas between 10 and 20 m^2/g after calcination in dry air at 1400°C [7,15]. Specific surface areas above 20 m^2/g could be maintained after ageing at 30 days in humid air at 1000°C [16]. A comparison of preparation methods showed that sol–gel synthesis (hydrolysis of alkoxides) followed supercritical drying gave the highest surface areas and also materials with highest purity of the hexaaluminate crystal phase. However, preparation by precipitation of carbonates gave almost the same results but was much easier to perform [15].

2. Experimental

2.1. Preparation of the hexaaluminate-based catalysts

For the synthesis of the pilot scale samples batches in the size of approximately 100–200 g were prepared wherefore the method based on precipitation of carbonates was chosen, cf. Ersson et al. [15] and Johansson et al. [3]. In short, nitrates of the final constituents are mixed and dripped slowly into a vigorously stirred flask with ammonium carbonate held constantly at a pH of 9. The precipitate was washed, dried and calcined in steps up to 1200°C, followed by wet ball-milling. Hereafter, precious metals were added to the slurry, if they were going to be present in the final composition. Finally, the monoliths were washcoated with the ball-milled slurry, dried and calcined up to 1200°C.

2.2. Synthetic gas mixture

The synthetic gas mixture described in Table 1 has been used for both the laboratory and the pilot scale experiments. Although the complexity of the gas mixture makes the experiments more complicated, it has been considered important to use a gas which includes all the main components of the real gas. The gas is mixed with air to the desired air to fuel ratio. In the pilot scale experiments, which are performed under close to adiabatic conditions, the inlet air temperature and the air to fuel ratio are used to control the temperature in the down-stream catalysts. In the laboratory scale experiments the levels of combustible components (CO, H_2, CH_4, C_2H_4) have been halved and balanced by N_2 to limit the heat of reaction. This, in combination with the small size of the monolith, results in that these tests are performed at close to isothermal conditions and the temperature of the surrounding furnace sets the catalyst temperature.

2.3. Laboratory scale equipment

The laboratory scale equipment consist of a quartz tube reactor mounted in a cylindrical furnace connected to seven Bronchurst Mass Flow Controllers and a water pump that facilitates to simulate a synthetic gas composition similar to the model gas given in Table 1. The experimental conditions are further described by monolith samples, 16 mm in diameter and 14 mm in length, temperatures between 100 and 950°C and gas hourly space velocities between 30 000 and 80 000 h^{-1}. The outlet of the reactor is connected to an online gas analysis system with detection of O_2, CO, CO_2, CH_4, H_2, NH_3, NO, NO_2 and total hydrocarbons. Inlet, outlet and furnace temperatures were monitored with N and P-type thermocouples. The laboratory reactor is further described by Johansson et al. [3,7].

2.4. Pilot scale equipment

The pilot scale testing on biomass derived fuels have been performed in a combustion rig connected to a pilot unit gasifier. In Fig. 1 the gasifier with the associated fuel feeding system, cyclone and high temperature filter is shown. The fuel system is pressurised with nitrogen gas and the fuel bin can hold approximately 0.4 m^3. A screw controls the amount of fuel coming into the gasifier with speed control in the bottom of the bin. Below the controlled screw the fuel feeding screw is situated, which holds a constant speed. The fuel system can handle pelletised fuel or chopped wood with a maximum size of 12 mm. Bed material is fed through

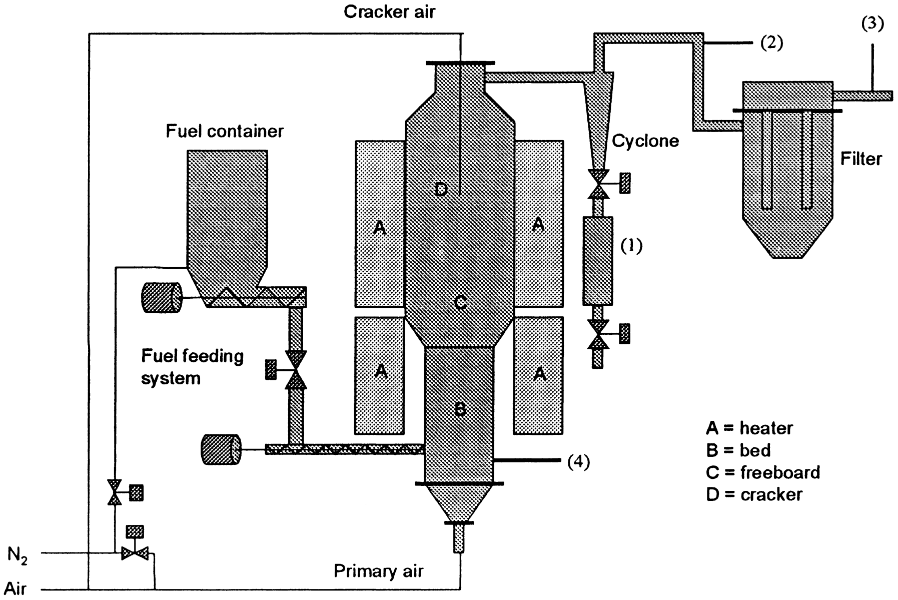

Fig. 1. Fluidised bubble-bed gasifier at TPS. Schematic drawing of the fuel feeding system, gasifier, cyclone and high temperature filters.

a speed controlled dosing equipment before it enters the fuel feeding system. The primary air to the gasifier is electrically heated. The gasification reactor itself is also electrically heated to minimise heat losses, thereby the heating value of the gas produced resembles a gas produced in a large scale gasifier. The height of the reactor is 2 m, excluding the top-cone and air distributor. Of this height, 0.6 m constitutes the fluid bed, with a diameter of approximately 0.2 m, the remaining 1.4 m is the freeboard, having a diameter of approximately 0.27 m.

The whole pilot unit is controlled via a PLC based control system. Since the fuel gas quality was not constant with time it was important with a rather fast sampling frequency wherefore all data was collected every 2 s. Except control of electrical heaters, the airflow and fuel feeding, the temperatures from thermocouples (type K) and the pressure drop over the gasifier is registered.

In the gasifier, gas corresponding to 20–30 kW can be produced. Down-stream of the gasifier particles are separated from the gas by a cyclone and a ceramic filter, which work at temperatures around 400°C. This gas is then led to a mixing chamber where the gas is mixed with the air and thereafter burnt in the combustion rig. When the model gas mixture was used in the pilot scale experiments, all the components of the dry gas was fed from a gas bottle and mixed with steam upstream of the air to fuel mixing point. The design of the combustor is shown in Fig. 2 and an enlargement of the mixing section is shown in Fig. 3.

The fuel used in the gasifier was pelletised sawdust with low nitrogen content (<0.1 wt.% of nitrogen on a dry basis). This fuel was chosen since it is a clean biofuel with low amounts of contaminants, such as sulphur and chlorine. To evaluate the conversion of ammonia to NO_x at different amounts of ammonia in the gas, concentrated ammonia gas was added to the fuel gas via a thermal mass flow meter through stainless steel pipes. The ammonia was added before the high temperature gas filter to ensure proper mixing between the ammonia and the fuel gas.

The pilot operates under essentially adiabatic combustion conditions, compared with the laboratory scale reactor that operates closer to isothermal conditions. The fuel gas is mixed with combustion air, which is electrically heated to enable the experiments to be performed with different inlet temperatures between 150 and 500°C. After mixing between the fuel gas and the combustion air the mixture enters the combustion chamber and reaches the catalyst section, where it is expected to ignite. The diameter of the catalyst seg-

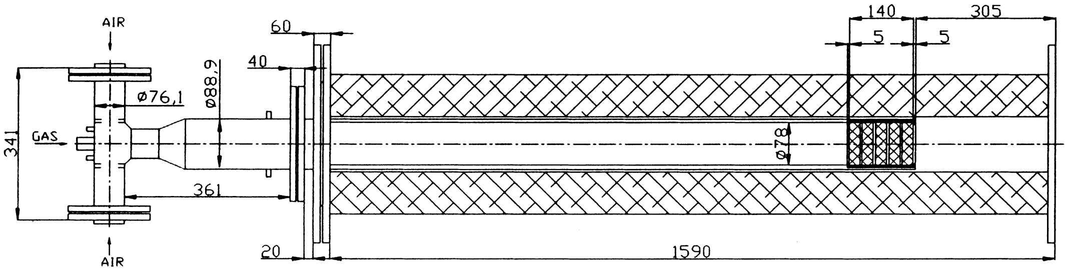

Fig. 2. Schematic drawing of the combustor, showing the catalysts' positions.

ments is 77 mm. One or several catalysts can be placed after each other. Total length of the combustion and mixing chamber from centre of the air pipe to the last catalyst is 1800 mm. The distance from the primary air flange to the outlet of the last catalyst can be varied but for all the experiments, which are reported in this paper, the distance was 1600 mm.

In applications of high temperature catalytic combustion both heterogeneous reactions on the catalyst surface and homogeneous gas phase reactions are important. An example of this is of course the hybrid combustor concept proposed by Catalytica Combustion Systems where the catalyst temperature is controlled through bypassing part of the combustible gas mixture through inactive channels [17]. Also in the case of a catalyst with all channels active high space velocity could result in incomplete combustion at the exit of the catalyst and the importance of homogeneous reaction in the channels of the catalyst must be considered. In these investigation the results where used both for comparison with laboratory scale experiments and with results achieved from computer simulations [18] wherefore the sampling probe for the gas analysis was positioned directly after the outlet of the last catalyst segment. Thereby the influence from homogenous reactions was minimised, even though not totally avoided.

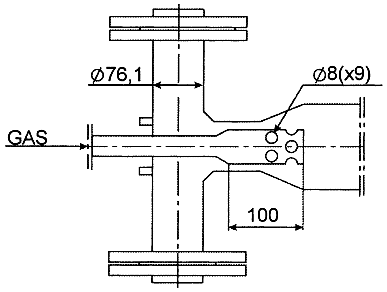

Fig. 3. Schematic drawing of the mixing section.

Due to the small scale of the gasifier even minor fluctuations in the fuel feeding rate had a direct effect on both the amount and the quality of the fuel gas fed to the gasifier. The average heating value of this gas was 4.5 MJ/$m_n{}^3$ but due to the fluctuations in the fuel feeding rate the heating value during the experiments varied with ±3% around this value. The flow rate of the fuel gas also had a variation of ±3% around the mean value with the higher flow rate corresponding to the higher heating value, thus both contributing to a higher fuel to air ratio and adiabatic temperature rise since the combustion air was kept constant. Apart from these fluctuations in the combustion temperature, which could not be avoided, the inlet air temperature was varied to perform experiments over a wider temperature range.

2.5. Catalyst configurations

A number of different combustion catalysts, either based on precious metals and active metal oxides, and combinations of these have been evaluated, both in the laboratory and pilot scale experiments. The preparation procedures of the LMHA and the PdLMHA catalysts are described in Section 2 of this paper while for the other catalysts the preparation procedure is proprietary information. The composition of the different catalyst segments is summarised in Table 2 and the combinations of catalyst segments used for the pilot scale experiments are summarised in Table 3.

The extruded hexaaluminate and the coated LMHA catalyst were also evaluated in the pilot unit without a

Table 2
Catalysts used for the pilot scale experiments

Catalyst	Cell density[a]	Carrier	Washcoat	Active phase	Preparation procedure
Pd	400 cpsi	Cordierite	γ-Al_2O_3, 185 g/l	Pd 5.6 g/dm^3	Proprietary, IFP
Pd, Pt	400 cpsi	Cordierite	γ-Al_2O_3, 190 g/dm^3	Pd 2.8 g/dm^3, Pt 2.8 g/dm^3	Proprietary, IFP
Extruded	300 cpsi	$Sr_{0.2}Mn_{0.8}BaAl_{11}O_{19}$			Proprietary, Süd Chemie
LMHA	400 cpsi	Cordierite	LMHA		[13] cf. experimental
PdLMHA	200 cpsi	Cordierite	LMHA	1.6 wt.% Pd	[13] cf. experimental

[a] Cell densities are based on the specifications given by the companies manufacturing the monolithic supports.

Table 3
Combinations of catalysts used for the pilot scale experiments[a]

Catalyst configuration No.	Segment 1	Segment 2	Segment 3	Segmenst 4	Segment 5
1	Pd	Pd	Pd	Pd	Pd
2	Pd, Pt	Pd, Pt	Pd, Pt	–	–
3	PdLMHA	Extruded	Extruded	–	–
4	PdLMHA	LMHA	LMHA	–	–

[a] The denomination is referring to Table 2. The length of each segment is 23 mm.

first precious metal-based segment. During these two tests three identical segments were used, each segment having a length of 23 mm.

The different catalyst configurations where evaluated under similar but not totally identical conditions. In Table 4 the conditions for the different tests are summarised for all the different catalyst configurations, both for the tests with biomass gasification gas and for the model gas mixture.

3. Results

In catalytic combustion the quality of the mixing between fuel and air is of utmost importance. Within the ULECAT project, further described in the paper by Le Gal et al. [8], a deviation from the mean value of maximum 5% have been set as a minimum requirement on the mixing quality. This should of course be seen as a maximum tolerable deviation and depending on the configuration harder restrictions could be set. Increasing the distance between the mixing point and the inlet of the catalyst of course increase the mixing quality and for the experimental pilot unit there are no space limitation as would be the case in a gas turbine application. The mixing quality between air and fuel can therefore be expected to be good, even with the rather simple design of the mixing section, cf. Fig. 3. This was also verified in experimental work under actual combustion conditions. Since the combustion was not complete during these experiments, significant levels of CO and THC remaining in at the exit of the cata-

Table 4
Conditions under which the different catalyst configurations were evaluated

Catalyst configuration No.	Fuel gas flow ($m_n{}^3$/h)	Combustion air ($m_n{}^3$/h)	Adiabatic combustion temperature[a] (°C)	Space velocity[b] (h^{-1})
1	15.7	50.0	1020	123000
2	14.0	48.0	980	193000
3	13.9	43.0	1030	177000
4	13.7	44.2	1010	180000

[a] Calculated on an inlet temperature of 300°C.
[b] Based on all catalyst segments.

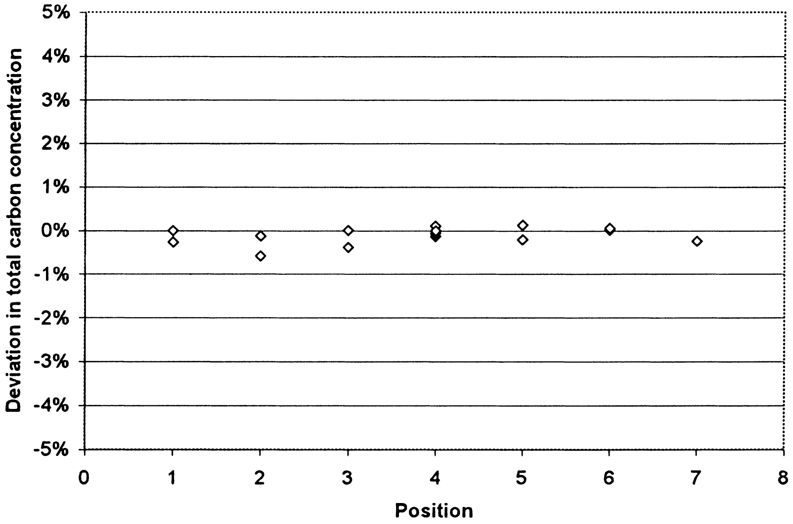

Fig. 4. Schematic drawing of the mixing section. Position 4 corresponds to the centre of the pipe and position 0 and 8 correspond to the wall.

lyst, the total carbon concentration (CO_2+CO+THC) was used as a measure for the fuel concentration. The deviation from the mean value was calculated and is shown in Fig. 4. It is clear that the deviation from the mean value is always less then 1%, i.e. the mixing quality is well within the required values.

The ignition temperature for the different catalyst configurations was measured by mixing air and fuel and slowly increasing the pre-heating temperature. For the catalyst configurations with a high precious metal loading the ignition temperature was determined only for the gas produced in the gasifier and ignition always occurred well below 200°C, cf. Table 5. For the two catalyst configurations that did not contain any precious metals no light off could be achieved below the maximum temperature experimentally evaluated. For the LMHA catalyst this temperature was limited to 510°C and for the extruded hexaaluminate this temperature was limited to 400°C. This does not imply that the light off temperature is lower for the extruded hexaaluminate, only that none of the hexaaluminate-based catalyst configuration reached light off temperature within the temperature range investigated. The ignition temperature for the PdLMHA catalyst was determined for both the gasification gas and the model gas mixture, resulting in a lower light off temperature for the latter.

Table 5
Ignition temperature for the different precious metal-based catalysts

	Gasification gas (°C)	Model gas mixture (°C)
Pd	140	Not determined
Pd, Pt	160	Not determined
PdLMHA	270	240

In the pilot unit the conversion of both CO and total hydrocarbon have been evaluated at various inlet temperatures. In Figs. 5–7 the emissions of CO and THC is shown as a function of the temperature in the last segment for the four different catalyst configurations. The experimental conditions were similar but not identical for the four evaluated configurations, cf. Tables 1 and 4. The temperature was in these experiments varied by changing the inlet temperature of the gas but it should be remembered that for the combustion of the gasified biomass the temperature also fluctuates due to the variations in heating value and fuel gas flow. At an inlet temperature of 300°C and adiabatic combustion temperature of 1000°C the ±6% variation gives rise to approximately ±40°C in combustion temperature.

3.1. Conversion of ammonia to NO_x

For the model gas mixture, which did not contain any ammonia, there was no significant formation of NO_x (<5 ppm). The gas from the gasifier contains low

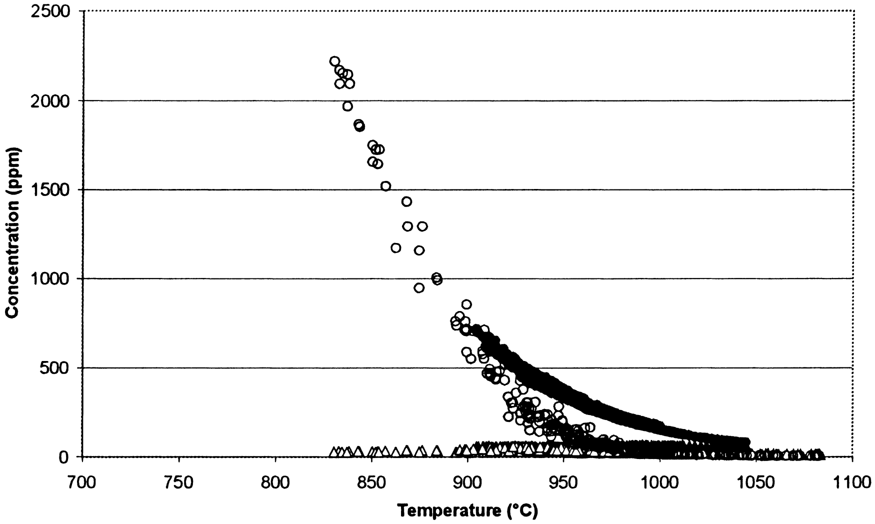

Fig. 5. CO (△) and THC (○) at different temperatures for catalyst configuration 1 (open symbols) and catalyst configuration 2 (filled symbols).

concentrations of nitrogen containing species, mainly in the form of ammonia but also, e.g. in the form of HCN. To be able to control the concentration of ammonia in the gas and minimise the influence from other nitrogen containing species a fuel with a low nitrogen content was used and ammonia was added to the gas. The conversion of ammonia to NO_x was determined from the increase in NO_x concentration in the flue gas in comparison with the added amount of ammonia. In Figs. 8 and 9 NO and NO_2 concentrations as well as the corresponding NO_x levels are shown for catalyst configuration 3 at two different levels of NH_3

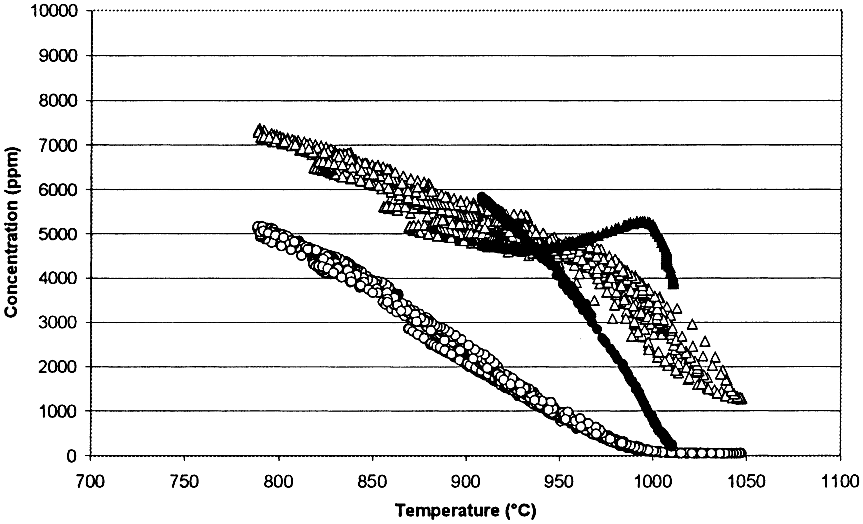

Fig. 6. CO (△) and THC (○) at different temperatures for catalyst configuration 3. Filled symbols mark the experiment using the model gas mixture. Observe the different scale on y-axis compared with Fig. 5.

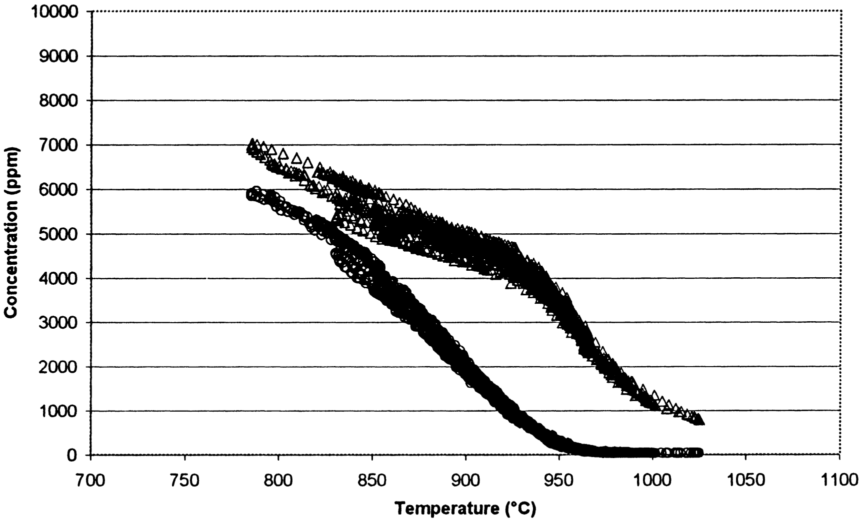

Fig. 7. CO (△) and THC (○) at different temperatures for catalyst configuration 4.

in the fuel gas, one corresponding to the background level of fuel-nitrogen and the other after addition of ammonia. For this configuration, having one precious metal-based stage followed by two segments without any precious metals, a significant effect of temperature on the relation between NO and NO_2 could be seen and especially in the case for the lower NH_3 concentration the concentrations of NO_2 are relatively high. This was not the case for the first catalyst configuration in which no significant effect of temperature on the NO and NO_2 concentrations could be seen and the NO_2 contributed to less then 10% of the total NO_x concentration. An important result of these experiments was that no significant effect of the temperature in the last catalyst segment on the total NO_x formation could be determined, i.e. no temperature dependence on the conversion of fuel nitrogen to NO_x could be determined.

For catalyst configuration 1, which contains segments with a high precious metal loading, a conversion of ammonia to NO_x close to the stoichiometric could be expected based on the laboratory scale experiments. This was also verified in the pilot scale experiments where 94% of the ammonia was converted to NO_x for the catalyst configuration with all segments based on precious metals, cf. Table 6. Ammonia conversion was also determined for the third catalyst configuration, which contained base–metal catalysts in the second and third stage, and this configuration resulted in a slightly lower conversion of ammonia to NO_x.

4. Discussion

4.1. Recollection of the laboratory scale results

4.1.1. Ignition of the gas in the laboratory scale set-up

In the laboratory study, a series of tests has been performed of the synthetic gas mixture over lanthanum and/or barium hexaaluminate catalysts, impregnated with palladium or platinum, or ion-substituted with iron, manganese or copper [7,16]. The temperature for 50% conversion was generally lower for carbon monoxide and hydrogen than for ethene. Methane was the least active. However, at high space velocities, i.e. above $50\,000\,h^{-1}$, the temperature for 95% conversion of carbon monoxide was higher than that of methane. As to the activity for ignition of carbon monoxide and hydrogen, palladium catalysts were generally the most active. Catalysts with a similar mole loading of platinum were slightly less active. The transition metal-substituted hexaaluminates were less active than the prepared precious metal catalysts. Transition metal-based catalyst are generally less active, although the apparent activity at temperatures

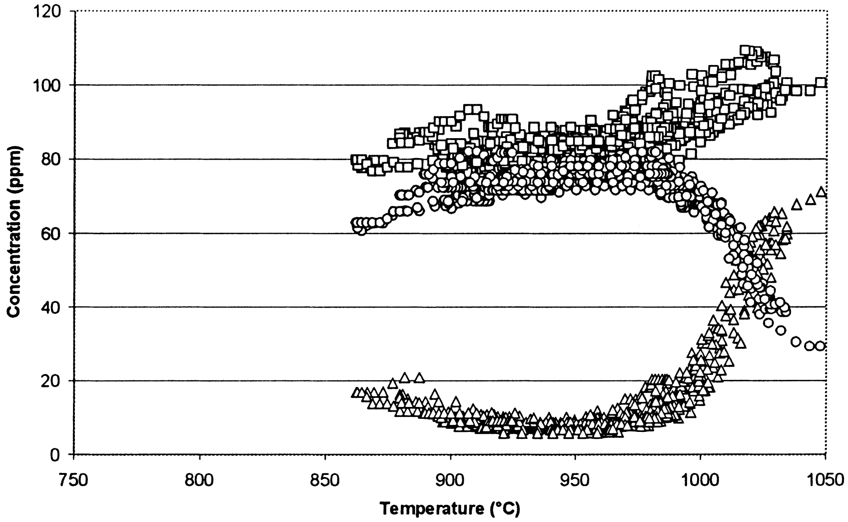

Fig. 8. Concentration of NO_x (□), NO (△)and NO_2 (○) in flue gas using catalyst configuration 3 at low NH_3-concentration (no addition of ammonia).

above 650–700°C is equal to that of the precious metals. At these temperatures, the onset of homogeneous reactions and mass transfer limitations are likely to level out the differences between the catalysts at the experimental conditions in these experiments, i.e. atmospheric pressures and relatively low gas velocities.

Several recent papers report on the state of the active palladium species over alumina [19–22] for methane combustion. It can be concluded that the high activity of palladium is due to the formation of highly active palladium oxide species. These species are stable up to the decomposition temperature of palladium oxide, approximately at 500–800°C, depending on gas

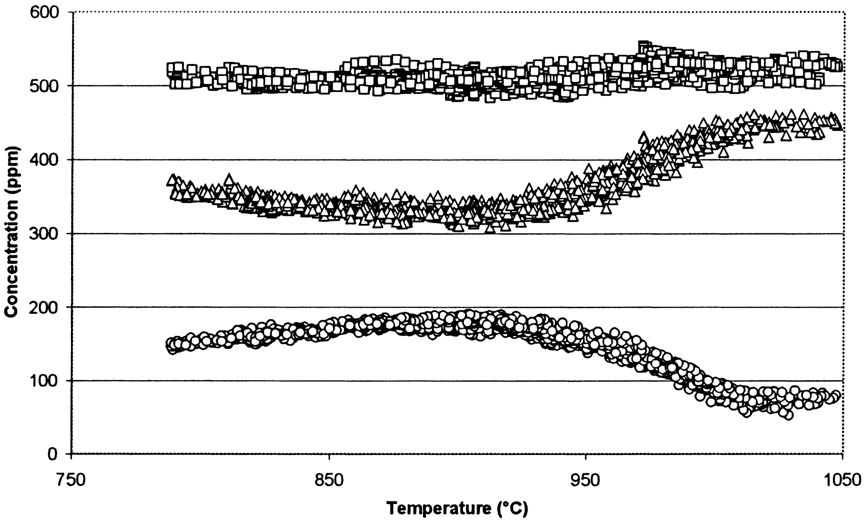

Fig. 9. Concentration of NO_x (□), NO (△) and NO_2 (○) in flue gas using catalyst configuration 3 at high NH_3-concentration (addition of ammonia).

Table 6
Conversion of ammonia to NO_x

Catalyst configuration	Added NH_3 (m_n^3/h)	Increase in NH_3 concentration (ppm)	Flue gas flow (dry) (m_n^3/h)	Increase in NO_x emission (ppm)	Conversion of added NH_3 to NO_x (%)
1	0.040	2840	59.3	637	94
3	0.025	1990	51.3	427	88

composition and pressure. The true state of the active sites has been suggested to consist of chemisorbed oxygen on palladium or palladium oxide present as a “skin” on palladium particles. In the tests described here, palladium catalysts are more active for methane conversion than platinum catalysts up to the temperature where palladium oxide decomposes and a plateau or decrease of the reaction rate is observed. At these temperatures, approximately, platinum catalysts are shown to be more active.

4.1.2. Selective ignition

The effects of varied palladium loading, gas hourly space velocity, and fuel composition (ethene, water and ammonia concentration) were studied by statistical evaluation of the temperatures needed for 10, 50 and 95% conversion, respectively [16]. The palladium series was compared to manganese-substituted and platinum-impregnated hexaaluminate samples. The results showed that gas hourly space velocity and palladium loading were the two most important factors in influencing ignition of carbon monoxide, hydrogen and methane. At very low loading of palladium, i.e. 0.1–0.4 wt.%, the temperatures (T_{10}, T_{50} or T_{95}) for ignition of methane were comparable to those of the sample with no palladium. However, the ignition of hydrogen and carbon monoxide was strongly affected by these small additions of palladium. Only at higher palladium loading, i.e. 0.8 wt.%, was the ignition temperature of methane significantly decreased. Hence, by selecting an appropriate palladium loading, it was possible to ignite the fuel gas selectively in the laboratory scale tests.

4.1.3. Circumventing the formation of NO_x from fuel-bound nitrogen

In the laboratory tests, temperature, space velocity, ammonia concentration and the catalyst composition primarily influenced the NO_x emission levels. Ignition of ammonia was observed at temperatures close to the ignition temperature of carbon monoxide and hydrogen. The onset of formation of nitrogen oxides was usually delayed, although high conversion rates could be measured over a fairly wide temperature regime. The conversion to nitrogen oxide varied as the inlet gas temperature to the reactor was increased. The formation of nitrogen monoxide (NO) was markedly higher than that of nitrogen dioxide (NO_2). The highest NO_2-levels were observed over base–metal catalysts at intermediate temperatures. The highest overall level of fuel-NO_x was observed over platinum-based samples, followed by palladium samples at intermediate temperatures, approximately 400–700°C. Manganese-substituted samples showed the lowest conversion of ammonia to NO_x. Moreover, an increase of the inlet ammonia concentration resulted in a slightly higher conversion of ammonia to molecular nitrogen, although the absolute NO_x outlet levels were higher.

At temperatures above 700–800°C, nitrogen oxide levels decreased markedly. Minimum conversions of ammonia to nitrogen oxides were approximately 30–50% over monolithic catalysts and even down to 12% in another reactor set-up (SCAR) [23].

It was concluded from the laboratory tests that the formation of nitrogen oxides from ammonia occurs via at least two mechanisms, namely a heterogeneously catalysed mechanism and a homogeneous mechanism. Both these mechanisms are likely to be very temperature-sensitive, similar to the SCR and the SNCR reactions. However, the level of potential reductants in the fuel gas is considerably higher than for SCR and SNCR conditions. Although the reduction of NO_x with N-free reductants is less efficient than with ammonia, species such as carbon monoxide and methane have been shown to reduce NO_x to molecular nitrogen [24]. Further, fuel-ammonia that has not yet reacted can reduce the already formed NO_x. Consequently, a method of lowering the fuel-NO_x

emissions could be to control fuel conversion and the temperature evolution in the combustor to reach an intermediate temperature regime where fuel-NO_x would be reduced. Similar schemes have been proposed in the early 1980s. The catalytic combustor could be a versatile tool to control the temperature profile.

4.1.4. Sulphur in the feed

In a previous paper [3], the influence of sulphur on the catalytic combustion of gasified biomass has been studied over precious metals and metal oxide based catalysts, namely $Pd/LaAl_{11}O_{18}$, $Pt/LaAl_{11}O_{18}$, $Pt/La_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}Al_{11}O_{19}$, $La_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}Al_{11}O_{19}$ and $LaMnAl_{11}O_{19}$. The samples were washcoated on cordierite monoliths and tested in a bench-scale reactor. Different concentrations of hydrogen sulphide as well as sulphur dioxide were added to the synthetic low-heating value fuel gas. The results show that all samples were deactivated to some extent by addition of sulphur, although the poisoning effect on catalytic combustion of each fuel component varied, depending both on the active phase and on the support, and generally reversible. The palladium catalyst was severely deactivated for combustion of methane, although the activity for carbon monoxide and hydrogen was more or less maintained. Platinum catalysts were more severely poisoned for carbon monoxide and hydrogen, but not for methane. Metal oxide catalysts were severely deactivated for all fuel components, especially for carbon monoxide, and the $La_{0.5}Ba_{0.5}Mn_{0.5}Fe_{0.5}Al_{11}O_{19}$-sample was irreversibly poisoned.

4.2. The pilot scale tests

Ignition temperatures for the precious metal-based catalysts with a high metal loading was reached well below 200°C. For the PdLMHA catalyst the ignition temperature was higher, and a difference was noticed between the model gas mixture and the real gasification gas. The observed difference in ignition temperature between the model gas mixture and the real gasification gas is likely to be due to the low concentrations of sulphur in the latter. However, even the highest ignition temperature is below typical compressor outlet temperatures.

For the precious metal-based catalysts high conversions can be achieved at outlet temperatures around 1000°C, corresponding to inlet temperatures around 300°C, cf. Fig. 5. For both the Pd and the Pd, Pt catalyst almost 100% conversion of CO is achieved already at moderate temperatures while the hydrocarbons, most likely only methane, needs the high temperature. Since the experiments using the Pd and the Pd, Pt catalyst were performed under slightly different linear velocity, air to fuel ratio and space velocity (SV) it is difficult to draw any conclusions on their relative activity for methane oxidation.

The results from configurations 3 and 4 when using the gasified biomass follow the same trend, cf. Figs. 6 and 7. It is clear that these two catalyst configurations, even though consisting of different active phases in stage two and three, have a similar selectivity for the different fuel components. The main difference between the results achieved for the two configurations is the shift towards slightly lower temperatures for configuration 4. Differences in the activity between the two catalysts cannot be excluded but also the different cell densities will influence the conversion, cf. Table 2. The effect of changing the cell density is shown in the comparison between these experimental results and the results from the mathematical model in the accompanying paper [18]. Since data are plotted against the temperature in the last segment the shift in temperature is also dependent on the differences in adiabatic combustion temperatures, cf. Table 4.

The large difference between the results achieved for catalyst configuration 3 with the gasification gas and the model gas mixture is most likely explained by the differences in fuel composition, cf. Fig. 6. Again differences in adiabatic combustion temperature can shift the conversion curves but the difference in shape is most likely due to the higher content of methane in the model gas mixture. The effect of low concentrations of sulphur in the gas produced in the gasifier has previously been shown to have an effect at low temperatures but is not likely to influence the conversion at high temperatures.

For the base–metal catalysts the levels of NO_2 were significant and for low ammonia concentration and low temperature even higher than the NO concentration. For these catalysts a strong dependence of temperature was seen on the NO_2–NO ratio but the total NO_x emissions was almost independent of temperature.

4.3. Comparison between pilot and laboratory scale tests

The ignition temperature follows the same trends in both pilot and laboratory scale experiments. Pd and Pt are more active than the base–metal catalysts, resulting in ignition below compressor outlet temperature for the former but not for the latter. Sulphur deactivates the latter which, in combination with the high space velocity, resulted in that no ignition was achieved over the catalyst within the temperature limits evaluated. The slightly higher ignition temperature for the PdLMHA catalyst in the gasified biomass could also be due to the presence of sulphur.

Carbon monoxide and hydrogen ignite at significantly lower temperatures than methane over precious metal-based catalysts in the laboratory scale tests. The base–metal catalysts showed a different behaviour with relatively low small temperature difference between the ignition of CO, H_2 and CH_4. At high GHSV, CO remained in the systems also after complete burnout of CH_4. The same trend was observed in the pilot scale tests. Over the precious metal samples, full conversion of CO (and H_2) was achieved at low temperatures while CH_4 remained at temperatures around 1000°C. This could be described as a selective ignition of CO and H_2 at intermediate temperatures. For the base–metal catalysts the situation is quite different. Here the levels of CO exceed the concentrations of hydrocarbons in the pilot scale experiments and high levels of CO are present as long as some hydrocarbons are remaining.

Both for the laboratory and pilot scale experiments the base–metal catalysts resulted in markedly higher levels of NO_2 compared with the precious metal-based catalysts, especially at moderate temperatures. In the laboratory scale experiments a significant difference in fuel-N conversion between precious and base–metal catalysts could be determined, the latter resulting in lower levels of NO_x. This difference has the potential to be used as a means to reduce the emissions of NO_x from fuels with a high level of fuel bound nitrogen. The high ignition temperature of base–metal catalysts demands a first stage with a precious metal containing catalyst under the experimental conditions considered here. This impeded the investigation of the potential reduction in NO_x over a non-precious metal catalyst configuration. A small decrease in conversion to NO_x was noticed also in the pilot scale experiments for the catalyst configuration with a first precious metal-based stage compared to the catalyst configuration with three precious metal-based stages. It is most likely that most of the ammonia was converted over the first stage and to reduce the NO_x levels the design has to be optimised. High inlet temperature and a small adiabatic temperature rise over the first stage (low conversion) could result in ignition in the following base–metal catalyst stage with most of the ammonia remaining. The optimisation of such a configuration has not yet been performed and it is an open question on how low NO_x levels that can be achieved. The laboratory scale experiments can however be taken as an indication on the potential of the technology.

5. Conclusions

Catalytic combustion of an LHV-gas produced from gasification of biomass has been performed in a pilot scale combustor. It was shown under actual combustion conditions that a good mixing quality between air and fuel could be achieved with a rather simple design of the mixing section.

Pilot scale tests verified deactivation by sulphur. Ignition could not be achieved over manganese-based catalysts in the pilot scale tests with real gasified biomass, even at a gas inlet temperatures of 510°C. Here, the low sulphur levels are expected to deactivate the catalysts. Over the different precious metal-based catalysts evaluated ignition of the low heating value gas could be achieved in the range 140–270°C. Hence, precious metal catalysts must be used for the first segment in the catalytic combustor.

NO and NO_2 were measured at the outlet of the reactor and it has been shown within the project that the NO_x formed almost entirely comes from fuel-bound nitrogen species, such as ammonia. The effect various non-precious metal-based combustion catalysts have on the fuel nitrogen conversion, resulting in a decreased conversion of ammonia to NO_x compared with precious metal-based catalysts, have been demonstrated in pilot scale experiments performed under essentially adiabatic combustion conditions. This has previously been demonstrated in laboratory scale experiments and the same trend as was shown in the laboratory scale was verified in the pilot scale experiments. In the laboratory scale experiments the conversion of ammonia to NO_x was between 30 and 90% but for the pilot scale experiments the lowest conversion of ammonia to NO_x achieved within this experimental series was 88%. This is far from targeted values and in fact higher than the conversion level expected for an ordinary diffusion flame but indicates that catalytic combustion could be an interesting alternative also for fuels with a high content of fuel bound nitrogen species.

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