Catalytic Combustion of Gasified Waste

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To my family
Front cover: Oil painting by Mary Kušar
Abstract

This thesis concerns catalytic combustion for gas turbine application using a low heating-value (LHV) gas, derived from gasified waste. The main research in catalytic combustion focuses on methane as fuel, but an increasing interest is directed towards catalytic combustion of LHV fuels. This thesis shows that it is possible to catalytically combust a LHV gas and to oxidize fuel-bound nitrogen (NH$_3$) directly into N$_2$ without forming NO$_x$. The first part of the thesis gives a background to the system. It defines waste, shortly describes gasification and more thoroughly catalytic combustion.

The second part of the present thesis, paper I, concerns the development and testing of potential catalysts for catalytic combustion of LHV gases. The objective of this work was to investigate the possibility to use a stable metal oxide instead of noble metals as ignition catalyst and at the same time reduce the formation of NO$_x$. In paper II pilot-scale tests were carried out to prove the potential of catalytic combustion using real gasified waste and to compare with the results obtained in laboratory scale using a synthetic gas simulating gasified waste. In paper III, selective catalytic oxidation for decreasing the NO$_x$ formation from fuel-bound nitrogen was examined using two different approaches: fuel-lean and fuel-rich conditions.

Finally, the last part of the thesis deals with deactivation of catalysts. The various deactivation processes which may affect high-temperature catalytic combustion are reviewed in paper IV. In paper V the poisoning effect of low amounts of sulfur was studied; various metal oxides as well as supported palladium and platinum catalysts were used as catalysts for combustion of a synthetic gas.

In conclusion, with the results obtained in this thesis it would be possible to compose a working catalytic system for gas turbine application using a LHV gas.

Keywords: Catalytic combustion; Gasified waste; LHV fuel; RDF; Biomass; Selective catalytic oxidation; NH$_3$; NO$_x$; Palladium; Platinum; Hexaaluminate; Garnet; Spinel; Deactivation; Sulfur; Poisoning
Sammanfattning

Avhandlingen behandlar katalytisk förbränning av förgasat avfall, ett så kallat lågvärdesbränsle, för gasturbintillämpning. Forskningen rörande katalytisk förbränning har i huvudsak varit inriktad på metan som bränsle, men intresset för användandet av lågvärdesbränslen har ökat. Avhandlingen visar att det är möjligt att katalytiskt förbränna ett lågvärdesbränsle och att oxidera bränslekvävet (NH₃) direkt till N₂ utan att bilda NOₓ. Första delen av detta arbete ger en beskrivning av systemet och definierar avfallet som bränsle, vidare ges en kort bakgrund till förgasning och en mer ingående beskrivning av katalytisk förbränning.


Sista delen av avhandlingen tar upp deaktivering av katalysatorer. I artikel IV sammanfattas och beskrivs olika deaktiveringsprocesser som kan ske vid katalytisk förbränning vid hög temperatur. I artikel V redovisas experimentellt hur olika metalloxider och ädelmetallbaserade katalysatorer påverkas av låga halter av svavel.

I slutsatsen visas att det med hjälp av de presenterade resultaten är möjligt att konstruera ett fungerande system för katalytisk förbränning av förgasat avfall i gasturbiner för elproduktion.

Nyckelord: Katalytisk förbränning, Förgasat avfall; Lägvärdesbränsle; Biomassa; Selektiv katalytisk oxidering; NH₃; NOₓ; Palladium; Platina; Hexaaluminat; Granat; Spinell; Deaktivering; Svavel; Förgiftning
The work presented in this thesis is based on the following publications, referred to by their Roman numerals. The papers are appended at the end of the thesis.


OTHER PUBLICATIONS

Other publications and conference papers on catalytic combustion and gasification not included in this thesis.

Papers


Conference contributions:

*Oral presentations:*

presentation/book of abstracts, 16th Canadian Symposium on Catalysis, Banff, Canada.


Poster presentations:


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1. INTRODUCTION

Background

Until recently most combustible wastes have been deposited in landfills, but new council directives [1999] from the European Parliament have increased the interest for the use of waste as a fuel. The objective of the directive is to prevent or reduce as far as possible negative effects on the environment from the landfiling of waste, by introducing stringent technical requirements for waste and landfills.

Combustion of waste both reduces the volume of waste that has to be deposited and utilizes the energy content of the waste. Hence, interest has increased for the use of waste as fuel. Normally waste is combusted directly in an incinerator and the product is mainly heat. In order to achieve a higher electricity/heat ratio an integrated combined cycle, IGCC, may be used. In an IGCC plant the waste is gasified and the produced gas is combusted in a gas turbine and the exhaust heat is utilised in a steam turbine [Bridgwater 1995]. The gas produced from the gasification step is a low heating-value, LHV, gas that mainly contains H₂, CO, and CH₄ as combustible components. The low heating-value of the gas, i.e. 15-20 MJ/kg, compared to natural gas, 48 MJ/kg, makes it more difficult to combust in a conventional gas turbine combustion chamber.

Catalytic combustion could be a solution for achieving a stable incineration of the gasified waste and furthermore catalytic combustion can achieve ultra-low emissions of hydrocarbons, carbon monoxide and nitrogen oxides. The main research in catalytic combustion focuses on methane as fuel, but an increasing interest is directed towards catalytic combustion of LHV fuels. The catalytic combustion chamber allows stable combustion outside the normal flammability limits, i.e. the adiabatic flame temperature can be lowered below the critical temperature for formation of thermal NOx, > 1500 °C. Moreover, a catalytic system performs with less thermo-acoustics variations during combustion.
The main problems in catalytic combustion using methane as a fuel is to ignite the fuel at the compressor outlet temperature and to find high-temperature stable catalysts, these are also important issues using a LHV gas. However, to succeed using a LHV gas deriving from waste or biomass, the fuel NO\textsubscript{X} formation from fuel-bound nitrogen compounds must be reduced to a minimum and catalysts that are resistant to poisoning must be found.

**The scope of this work**

The objective of this thesis has been to investigate catalyst materials for catalytic combustion of gasified waste or biomass-like fuels for gas turbine application producing electricity. Waste material could possibly contain any element from the periodic table. In this thesis the main issues have been sulfur and fuel-bound nitrogen, other contaminating elements are considered to be remain in the ashes trapped in the cyclone or filters after the gasification. The thesis can be divided into three main parts. The first part of the thesis gives a background to the system. It defines waste, shortly describes gasification and more thoroughly catalytic combustion.

The second part of the thesis, papers I and II, is focused on the development and testing of novel catalysts for catalytic combustion of LHV gases. In paper I, suitable ignition catalysts and high-temperature materials are tested for LHV gases and in paper II pilot-scale tests are carried out to prove the potential of catalytic combustion using real gasified waste.

Paper III investigates the possibilities of selective catalytic oxidation for decreasing the NO\textsubscript{X} formation from fuel-bound nitrogen using two different approaches: fuel-lean and fuel-rich conditions.

The last part deals with deactivation of catalysts. In paper IV the different phenomena of deactivation for a catalytic system present in a gas turbine combustor are reviewed and discussed. Paper V examines the poisoning effect of low amounts of sulfur in the catalytic combustion of gasified waste on various metal oxides as well as supported palladium and platinum catalysts.
2. **Waste Material**

Waste material is a very wide definition of almost anything. According to the EU definition, waste is “any substance or object in the categories set out in Annex 1 which the holder discards or is required to discard”. Waste is therefore categorized into many different classes. The definition of waste has a central role. This is what ultimately decides whether a substance is to be handled according to the relevant rules on environmental protection [RVF 2003a]. The definition of waste is the same throughout Europe, and it is only the Court of Justice of the European Communities that has the right to define it in detail. There is a large number of judgements about the definition of waste; their common feature is that the definition is very broad and is supposed to be.

In the present thesis only combustible waste is considered. As can be seen in fig 2.1, both for the world’s and Sweden’s energy consumption the use of combustible renewables and waste is of importance. The picture is somewhat different in most European countries with less use of biomass, however the amounts of combustible waste are in the same range and are increasing for every year.

![Figure 2.1](image)

*Figure 2.1 The energy consumption (% by fuel) in the world and in Sweden in 1999 [IEA 2002]*
In 2001, the use of biomass in Sweden amounted to over 97 TWh [STEM 2002]. These fuels mainly consist of:

- Wood fuels
- Black liquors in pulp mills
- Peat
- Straw and energy grasses
- Waste

Waste is included in the 97 TWh. Biomass is regarded as CO₂ neutral and is a renewable fuel. Biomass also releases carbon dioxide as it is combusted, but the plants need CO₂ to grow, giving a closed carbon cycle. All the CO₂ released during the combustion of biomass materials is recaptured by the growth of these same materials. Unlike fossil fuels, there is no net increase in carbon dioxide released into the atmosphere when biomass is combusted. Combustible waste material can be considered as semi-CO₂ neutral since it contains large amounts of original biomass, however it also contains plastics made from fossil fuel.

Waste material has been used for district heating production since the 1970s and in 2001 it provided 5 TWh of energy in Sweden. The new regulations under which combustible waste must be separated from other waste materials are coupled with the ban on disposing unsorted combustible waste to landfill. Since January 1st 2002, landfill disposal has been taxed at a rate of 288 SEK/tonne of waste. Waste sent for combustion is exempted from the tax, however the ash is taxed [STEM 2002].

The waste material in this work has been defined twice, first in 1999, the waste material consisted of 50-60% paper waste, 30-40% plastics mainly polyethene, 10% RDF and about 2-3% forest residues. Later in 2001 the amount of RDF in the combustible waste increased to about 40%, due to the new legislation. However as can be seen in Table 2.1 the differences in composition are not very significant the largest difference is the higher amount of ash in the waste containing 40% RDF.
Refuse-derived fuel, RDF, is a result of processing municipal solid waste, MSW, to separate the combustible fraction from the non-combustibles, such as metals and glass. RDF is predominantly composed of paper, plastic, wood and kitchen or yard wastes, and has a higher energy content than untreated MSW. Household waste mostly consists of renewable material – biofuel. It thus contributes only marginally to an increase in the greenhouse effect when it is incinerated.
3. COMBUSTION

Incineration has a long history as a method for taking care of waste from households, industries and other activities in society. Special plants for incinerating household waste started being developed in Europe at the end of the 19th century. The first waste incineration plant in Sweden started up in 1901 in Lövsta outside Stockholm. However, it took a long time before incineration plants started being expanded. Any incineration that did occur took place in open fires on rubbish heaps or in simple furnaces.

Today combustion in ordinary incinerators of biomass and related materials is widely practised commercially to produce heat and power. The technology is commercially available and presents a minimum risk to the investor. In Sweden today it is clear that the manufacture of more environmentally friendly products, source separation of products such as batteries, and environmental protection initiatives made at the plants have together produced results. Discharges of mercury and cadmium decreased by 99% between 1985 and 1999. Discharges of lead have been reduced from 25000 kg a year to 35 kg a year, and zinc from 54000 to 90 kg a year. The emissions of dioxins to air are barely 3 g a year, compared to 90 g a year in 1985. At the same time, waste incineration has increased by 35% and energy generation from waste has more than doubled [RVF 2003b].

However, even though the incineration technique has improved enormously, the overall electrical efficiencies are low. New efficient and even more environmentally friendly techniques are available, such as the integrated gasification combined cycle that could be used for energy production from waste.

Integrated gasification combined cycle

The advantage with the integrated gasification combined cycle, IGCC, is the high electrical efficiency. First the chemical energy in the biomass or waste is converted to a gas in a gasifier, the obtained gas is then combusted in a
gas turbine producing electricity, the hot exhaust gases from the turbine are further utilized in a steam turbine producing even more electricity. The integration of gasification and combustion/heat recovery ensures a high electrical efficiency of 40 - 50%, based on the incoming LHV gas [McKendry 2002]. The IGCC technique has been demonstrated in the Värnamo plant in Sweden for over 3600 h with a range of different biomass fuels using a circulated fluidized bed gasifier [Ståhl 2000]. Fig. 3.1 shows the IGCC concept with a gas turbine using catalytic combustion.

![Figure 3.1 The IGCC concept for gasified waste](image)

**Gasification**

In order to use solid waste as fuel in a gas turbine it has to be converted into a combustible gas. Gasification is a process converting a solid fuel into a combustible gas mixture by partial oxidation of the waste/biomass at high temperatures, normally in the range of 800 to 900 °C. It is a thermochemical process including drying, pyrolysis and the gasification itself. The gas produced contains a mixture of H₂, CO, CO₂, CH₄, and small amounts of higher hydrocarbons such as ethane and ethene, H₂O, and N₂ if air is used as oxidizing agent. The partial oxidation can be carried out using air, oxygen, steam or a mixture of these [Bridgwater 1995]. Air gasification produces a poor quality gas in terms of the heating value, about 4-7 MJ/Nm³ depending on the fuel. Using oxygen, the gas from the gasifier is not diluted by nitrogen and a higher heating value can be obtained. This thesis is based on the use of a synthetic gas simulating the gas from an air-blown waste gasification. In Table 3.1 the composition of gasified waste containing 40% RDF is shown, the gas utilized in paper II, and the synthetic
gas mixture simulating gasified waste used for the lab-scale catalytic combustion experiments.

Table 3.1. The composition of the gasified waste containing 40% RDF from the pilot-scale gasifier, calculated with an airflow of 53 Nm$^3$/h into the gasifier, and of the synthetic gas used in the lab-scale experiments, both with $\lambda$=3.3 (from paper II)

<table>
<thead>
<tr>
<th>Gas compound</th>
<th>Gasified RDF (%)</th>
<th>Synthetic gas (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>71.7</td>
<td>67.9</td>
</tr>
<tr>
<td>O$_2$</td>
<td>16.5</td>
<td>18.1</td>
</tr>
<tr>
<td>H$_2$</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>CO</td>
<td>2.9</td>
<td>3.7</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.1</td>
<td>3.5</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.72</td>
<td>1.2</td>
</tr>
<tr>
<td>C$_2$-C$_3$</td>
<td>0.25</td>
<td>0.0</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>1.34</td>
<td>3.0</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>0.002</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The choice of gasification technology depends on the size of the unit, i.e. the fuel capacity. Many gasification reactor types have been developed, examples are: downdraft, updraft, co-current, counter-current and different kinds of fluidized bed technologies. The circulating fluidized bed, CFB, gasifier has been extensively developed for gasification of the biomass type of fuels [Bridgwater 1995].

The fluidized bed unit can be either atmospheric or pressurized. Atmospheric CFB gasifiers have proven to be reliable with a variety of feedstocks and are easy to scale up from a few MW up to 100 MW. Pressurized fluidized bed systems are advantageous in IGCC applications since there is no need to compress the fuel gas prior to the gas turbine combustor chamber; pressurized fluidized bed systems are however considered more complex and are primarily attractive for large-scale applications [Bridgwater 2003].

The last step in the gasification is fuel cleaning processes. Cyclones and filters separate large particles and tar cracking by high temperature or cracking catalysts is used to decompose heavy condensable hydrocarbons
into lighter hydrocarbons. Alkali metal compounds exist in the vapour phase at high temperatures and have to be removed, either by filters at lower temperatures or by water scrubbing, since alkali metals may cause high-temperature corrosion of turbine blades; the alkali concentration must not exceed 0.1 ppm at the entry to the turbine. Therefore alkali metals that normally might be possible poisons to a catalyst are not considered.

Other pollutants from the gasification can be lowered by fine-tuning the gasification process, for example by using dolomite or other active compounds to absorb sulfur and chlorine. Further wet scrubbing lowers the amount of particles, fuel-bound nitrogen, tars, water and chlorine. In conclusion the gasification techniques for use of biomass are highly developed and it is possible to obtain a clean gas entering the gas turbine and to the catalyst. For catalytic combustion the fuel-bound nitrogen and sulfur species are the main pollutants that have to be considered when developing a catalyst or catalytic system.
4. **GAS TURBINE COMBUSTION**

There are two types of gas turbines; gas turbines for stationary power production and mobile gas turbines for transportation. Stationary gas turbines with integrated gasification of waste for energy production will only be considered here. The main components of a gas turbine are the compressor, the combustion chamber and the turbine driving a generator producing electricity. A schematic view of a gas turbine unit is given in Fig. 4.1 The work in such gas turbine follows the Brayton cycle. The air is compressed in the compressor, increasing the pressure as well as the temperature of the air. The hot and pressurized air is mixed with the fuel in the combustion chamber of the gas turbine. Before the large energy released in the combustion is converted into mechanical energy by expansion in the turbine it has to be mixed with by-pass air to cool the gas stream to a suitable turbine inlet temperature. A modern gas turbine can withstand temperatures up to 1400 °C. The work produced in the turbine is used to power the compressor and to produce electricity in the generator.

![Figure 4.1 A schematic view of a conventional gas turbine unit](image)

The design of the gas turbine and the different components varies and will not be described here, for further reading see Lefebvre [1983], Cohen et al
However, since gasified waste is a low heating-value fuel, the fuel flow is much higher, up to 20% of the total combustion mass flow, compared to natural gas that only makes up a few percent of the airflow. A great desire is to use the gas turbine for multi-fuel application, but the large fuel flow of gasified waste or biomass leads to a discrepancy between the compressor and the turbine [Lefebvre 1983]. For small gas turbines with lower pressure ratios, from micro turbines of 50 kW to a few MW, it is possible to increase the efficiency of the gas turbine by heat exchanging the compressor inlet gases with the hot gases from the turbine. This recuperative method works only for gas turbines with low pressure ratios, i.e. the compressor work and the temperature increase in the compressor have to be relatively low.

**Emissions from combustion**

Theoretically, complete combustion of a hydrocarbon with oxygen results in the production of heat and the only by-products are water and carbon dioxide. However, all combustion processes produce emissions and the driving force to reduce them is mainly due to legislation. In combustion processes various kinds of emissions are formed, some due to incomplete combustion of the fuel, like hydrocarbons, HC, and carbon monoxide, CO. Other emissions are formed as a result of the combustion process itself, like the formation of carbon dioxide, CO\textsubscript{2}, and nitrogen oxides, NO\textsubscript{x}. Furthermore, emissions like sulfur dioxides, SO\textsubscript{x}, and hydrogen chloride, HCl, and dioxins are emissions that may be formed in the combustion process depending both on the fuel and the combustion process itself.

If the combustion is incomplete the exhaust gases will contain hydrocarbons and carbon monoxide. The production of these gases not only lowers the overall efficiency of the combustion but also causes harmful emissions. Carbon monoxide is extremely poisonous even in small concentrations as it forms strong bonds to the hemoglobin molecules in the blood.

Hydrocarbons, often called unburned hydrocarbons, UHC, or total hydrocarbons, THC, in the effluent are a wide definition of compounds that
may be carcinogenic, like the chlorinated polyaromatics such as dioxins. The hydrocarbons may also interact with nitrogen oxides and sunlight forming ground-level ozone. For example, CH₄ is also a greenhouse gas, much worse than CO₂.

Carbon dioxide was for a long time considered as a harmless product of combustion, today it is know as a greenhouse gas contributing to heating of the atmosphere. The formation of CO₂ is impossible to avoid when using hydrocarbons as fuel, since it is one of the main reaction products. To reduce the amount of CO₂ released to the atmosphere the combustion processes can be made more efficient or new technology capturing CO₂ for storage in for example old oil or gas wells may be used. However, the use of renewable fuels is the most efficient way of reducing CO₂ emissions, since they are considered CO₂ neutral.

Nitrogen oxides are harmful pollutants from the fuel combustion process. They contribute to the acidification of lakes and cause forest depletion. The acidification of water might lead to dissolution of heavy metals, which normally remain insoluble at higher pH values. These metals can pass into the food chain and into the drinking water. NOₓ are also a strong contributor to the formation of photochemical smog and affect the ozone balance in the stratosphere.

The increasing concern for protection of the environment has lead to more stringent regulations with respect to the above-mentioned emissions deriving from the combustion process. This calls for the development and implementation of new combustion technologies and therefore it is of vital importance to identify and study the mechanisms of formation of these pollutants in order meet the future emission standards at a reasonable cost.

**Formation of nitrogen oxides**

Nitrogen oxides or NOₓ, is the common name used for both nitrogen oxide, NO, and nitrogen dioxide, NO₂. There are four recognized routes for the formation of NOₓ, namely:

- Oxidation of molecular nitrogen in the air via the thermal NOₓ mechanism.
• The prompt NO\textsubscript{X} mechanism.
• Through the formation of N\textsubscript{2}O to NO\textsubscript{X}.
• Oxidation of nitrogen-containing organic compounds in the fuels through the fuel-bound NO\textsubscript{X} mechanism.

**Thermal NO\textsubscript{X}**

Thermal NO\textsubscript{X} is formed from air at temperatures above 1400 °C when the nitrogen and oxygen molecules react and form NO\textsubscript{X} through a radical mechanism postulated by Zeldovich, and later developed into the Zeldovich mechanism [Glassman 1996].

\[
\begin{align*}
O + N_2 & \leftrightarrow NO + N \quad (1) \\
N + O_2 & \leftrightarrow NO + O \quad (2) \\
N + OH & \leftrightarrow NO + H \quad (3)
\end{align*}
\]

The oxygen radical in reaction (1) is mainly formed from water, some radicals are also supposed to come from dissociation of O\textsubscript{2}. The formed N radical reacts further with oxygen in the air producing NO and another O radical (2). The formed N radical may also react with the OH radical deriving from the water and form NO as in reaction (3). At temperatures above 1500 °C the formation of thermal NO\textsubscript{X} is significant and increases even more at higher temperatures.

**Prompt NO\textsubscript{X}**

Another way of producing NO\textsubscript{X} is through the so-called prompt NO\textsubscript{X} formation. It is formed from reactions between hydrocarbon radicals and nitrogen molecules forming hydrogen cyanide, which is further oxidized into NO. Formation of prompt NO\textsubscript{X} only takes place in hydrocarbon-containing flames. Prompt NO\textsubscript{X} is mostly formed in slightly rich flames. Several mechanisms have been proposed describing the formation of prompt NO\textsubscript{X}, where the most common involves a chain of radical reactions between the hydrocarbon fuel and nitrogen in air. The reactions can be shortly written as following the two reactions (4) and (5):

\[
CH + N_2 \rightarrow HCN + N \quad (4)
\]
\[ N + OH \rightarrow H + NO \] \hspace{1cm} (5)

Prompt NO\(_x\) formation is not avoided by lowering the combustion temperature, as is the case for the thermal NO\(_x\), since the rate of formation is not especially temperature dependent. As opposed to thermal NO\(_x\) its main contribution to the total NO\(_x\) is below 1300 °C, and the only method to avoid its formation is by lowering the amount of hydrocarbon radicals formed [Glassman 1996].

**Nitrous oxide**

Nitrous oxide, N\(_2\)O may form NO through the following reaction mechanism involving radical oxygen:

\[ O + N_2O \rightarrow 2NO \] \hspace{1cm} (6)

However, N\(_2\)O is primarily formed via a third body, M, as in reaction (7):

\[ N_2 + O + M \rightarrow N_2O + M \] \hspace{1cm} (7)

The most important N\(_2\)O removal steps are:

\[ H + N_2O \rightarrow N_2 + OH \] \hspace{1cm} (7)

\[ O + N_2O \rightarrow N_2 + O_2 \] \hspace{1cm} (8)

Nitrous oxides are not stable at high temperatures and therefore the contribution in flame combustion is insignificant, however it is significant at lower temperatures and in lean premixed laminar flames [Glassman 1996].

**Fuel NO\(_x\)**

LHV fuels like gasified waste or biomass contain significant amounts of fuel-bound nitrogen. Fuel NO\(_x\) is formed when fuels containing nitrogen are combusted under lean conditions. During the combustion of these N-containing compounds they thermally decompose prior to the combustion zone. Hence, precursors for NO\(_x\) formation are created. These are compounds or radicals with low molecular weight containing nitrogen, NH\(_3\), NH\(_2\), NH, HCN, CN, etc. The oxidation of these compounds to NO\(_x\) is
rapid. The mechanisms for forming fuel NO\textsubscript{x} are shown in some of the following radical reactions [Glassman 1996]:

\[ NH_x + O_2 \rightarrow NO + \ldots \]  \hspace{1cm} (9)

\[ CN + O_2 \rightarrow NO + \ldots \]  \hspace{1cm} (10)

\[ NH + H \rightarrow N + H_2 \]  \hspace{1cm} (11)

\[ NH + OH \rightarrow N + H_2O \]  \hspace{1cm} (12)

\[ NH + H \rightarrow N + H_2 \]  \hspace{1cm} (13)

The formed N radicals can react further, according to the thermal NO\textsubscript{x} mechanisms (1)-(3) to form NO\textsubscript{x}. In fuel-rich systems the fuel nitrogen intermediate not only reacts with the oxidizing species, but also competitively with NO to form N\textsubscript{2}. This is the reason for NO\textsubscript{x} yields being lower in fuel-rich systems. The high yields of NO\textsubscript{x} in fuel-lean systems are a dilemma, since it is desirable to have lean operation to reduce hydrocarbon and carbon monoxide emissions or, like in the catalytic gas turbine environment, to lower the reaction temperature to minimize the formation of thermal NO\textsubscript{x}. In paper III, selective catalytic oxidation of the nitrogen-bound fuel is investigated for both fuel-lean and fuel-rich environments.
Low emission technologies for gas turbine combustors

Gas turbines have continuously been developed towards higher efficiencies and lower emissions. There are a number of different combustion approaches that aim at achieving low emissions, especially for NO\textsubscript{x}. The following gas turbine combustor concepts are all working options for low emission [Cohen et al 1996]: lean premixed combustion, rich burn–quick quench–lean burn, and water or steam injection together with catalytic combustion. Catalytic combustion will be discussed in the next chapter (V).

Lean premixed combustion

Lean premixed combustion can achieve thermal NO\textsubscript{x} levels down to 10 ppm. The fuel is mixed with air prior to the combustion zone very close to the flammability limits, hence the temperature of the flame is kept at a minimum, i.e. the adiabatic temperature rise is low at temperatures where the formation of thermal NO\textsubscript{x} is low. However at ultra-low levels of NO\textsubscript{x} this technique has drawbacks, it is very sensitive operating so close to the flammability limits, instabilities may occur, giving rise to thermal acoustic phenomena that can damage the turbine.

Rich burn – Quick quench – Lean burn

The rich burn–quick quench-lean burn, RQL, technique first combusts the fuel in a rich environment with excess fuel, then air is added creating a strong turbulence mixing the air and the fuel, which is burned lean in the last zone. The rich conditions ensure a low thermal NO\textsubscript{x} level zone, while the mixing of a large excess of air lowers the adiabatic temperature, as for the lean premixed combustion, avoiding the thermal NO\textsubscript{x} formation. RQL is more efficient for N-containing fuels, like gasified waste, which can be reduced in the fuel-rich stage compared to the other techniques. The problem with this concept is its complexity, switching from rich to lean, this must be done very fast to prevent high-temperature zones, which lead to the formation of thermal NO\textsubscript{x}.

Water or steam injection

Another technology is to introduce water into the gas turbine, which decreases the flame temperature and significantly lowers the formation of
thermal NO\textsubscript{x}. It is possible to further decrease the NO\textsubscript{x} emissions by further increase of the water to fuel ratio, however this is accompanied by an increase of the CO and hydrocarbon levels.

**Treatment of the exhaust gases**

For combustion processes in general a common way is to clean the exhaust gases downstream the combustor chamber. There are many techniques that have been developed, but the far most important ones are selective catalytic reduction, SCR, and the selective non-catalytic reduction, SNCR. As the names suggest the SCR technique uses a catalyst to promote the reaction between added NH\textsubscript{3} and the NO\textsubscript{x} in the stream forming N\textsubscript{2}. The SNCR technique operates at high temperatures, between 900 and 1100 °C, where ammonia or urea reacts with the NO\textsubscript{x} to form N\textsubscript{2} and water. The drawbacks of these so-called tail-end techniques are that they are both expensive and require good process control to avoid ammonia slips. SCR is the most effective of the two and can achieve ultra-low NOX emissions, down to 10-20 ppm, however at high costs [Farrauto and Bartholomew 1997].
5. CATALYTIC COMBUSTION

Catalytic combustion offers an alternative way of producing energy. Not only for methane as fuel, but a wide range of concentrations of hydrocarbons can be oxidized over a suitable catalyst. In order to understand the advantages and problems with catalytic combustion, it is valuable to discuss the difference between traditional flame combustion and catalytic combustion, or more specifically high-temperature catalytic combustion, which here refers to gas turbine applications. However, other applications might be considered, like radiant heaters, domestic boilers etc, but they are not discussed in this work.

Catalytic combustion in gas turbines

In the traditional flame combustion system compressed air and fuel are mixed, then combusted in the combustion chamber with a flame, the hot gases are expanded and drive the turbine; the flame temperatures may easily rise to 1500-2000 °C, where formation of thermal NOx occurs. Cooling of the hot gases with by-passed compressed air is necessary to reduce the temperature to 1200-1500 °C before delivery to the turbine inlet, the temperature range depending on the turbine.

In a catalytic combustor there is no flame present, the air and fuel are well mixed before entering the catalyst. The fuel-air mixture is ignited over the catalyst, also outside the flammability limits. The combustion is carried out at lower temperatures, calculated for the inlet temperature of the turbine. In addition other emissions like carbon monoxide and unburned hydrocarbons are low due to the stabilized combustion over the catalyst.

The mechanisms involved in catalytic combustion are complex and depend on many parameters, like temperature, pressure and the type of catalyst. The general reaction paths for catalytic combustion are, however, well established [Lee and Trimm 1995], see fig. 5.1 As the temperature is increased, the oxidation starts at a temperature depending on the fuel (hydrocarbon) and the catalyst. A further increase in temperature leads to
an exponential increase in the reaction rate, area B, to a point where the heat generated by the combustion is greater than the heat supplied, then the reaction becomes mass-transfer controlled, area C, until the reactants in the fuel are depleted, area D. In this area both heterogeneous reactions on the catalyst surface and homogeneous reactions in the gas phase proceed simultaneously [Arai and Machida 1991].

![Figure 5.1 Conversion vs. temperature in catalytic combustion](Lee and Trimm 1995)

One of the most important factors in catalytic combustion is the light-off of the fuel, the kinetics of catalytic combustion are only relevant to parts A and B in the figure. After the ignition, mass and heat transfer are the important parameters. The geometry of the catalyst together with the porosity have much more effect in this region, C. The reaction rapidly approaches complete conversion, and the heat generated in the combustion results in a significant increase in catalyst temperature. Therefore the stability of the catalyst is of major importance in high-temperature catalytic combustion. One of the crucial problems is to suppress sintering of the oxide supports, this will be further discussed in chapter VI.
Requirements for a catalytic combustor

The technique is very attractive and has been proven by several independent pilot-scale tests, which have reported single digit emissions of NO\textsubscript{x}, CO and hydrocarbons for combustion of methane [Schlatter et al 1997, Ozawa et al 1999, Carroni et al 2002, Kajita and Dalla Betta 2003]. However, there are problems that have to be solved. Prasad et al [1984] have summarised the properties needed for a suitable combustion catalyst:

- Ignition of fuel-air mixtures at as low temperature as possible, i.e. at the compressor outlet temperature, 350 °C.
- The catalyst activity should be sufficiently high to maintain complete combustion at the lowest and highest value of mass throughput.
- The support should maintain moderately high surface area under the specific operating conditions, up to 1350 °C.
- The support should have a large surface area, low pressure drop, good thermal shock resistance and allow high working temperatures.
- The catalytic system should be stable enough to allow prolonged use at these high temperatures.

These statements were made 20 years ago and are still very much legitimate today. Carroni et al [2002] have recently stated the demands on a catalytic combustion chamber in a gas turbine before it may be a competitor to traditional low-emission combustors, see Table 5.1. Using a LHV gas as fuel it is of extra importance that the catalyst be resistant to poisoning otherwise the same requirements are valid as for natural gas.
Table 5.1 Requirements for a catalytic combustion chamber in gas turbines [from Ersson 2003a]

<table>
<thead>
<tr>
<th>Type</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature</td>
<td>350-450 °C</td>
</tr>
<tr>
<td>Exit temperature</td>
<td>1500 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>8-30 bar</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>&lt;3 %</td>
</tr>
<tr>
<td>Mixedness</td>
<td>80-85 %</td>
</tr>
<tr>
<td>Ambient condition variations</td>
<td>-25 - +40 °C</td>
</tr>
<tr>
<td>Working life</td>
<td>&gt;8000 h</td>
</tr>
<tr>
<td>Poisons</td>
<td>Resistant to sulfur and others</td>
</tr>
<tr>
<td>Thermal shocks</td>
<td>&gt;500 °C/s</td>
</tr>
<tr>
<td>Multi fuel capability</td>
<td>Natural gas / Liquid fuels</td>
</tr>
<tr>
<td>Size restrictions</td>
<td>Typically 300 mm length 180 mm diameter</td>
</tr>
</tbody>
</table>

**Designs of catalytic combustors**

As can be studied in Table 5.1, there are many demands to fulfil, the most critical one being that no catalytic material has been found that can withstand the maximum temperature for real long-time operations. Hence no single material can fulfil all these demands on a catalyst for catalytic combustion. For that reason, it is convenient to divide the combustion chamber into three different temperature zones with different requirements on the catalyst. First the low-temperature catalyst, that has to be highly active and ignite the fuel at the compressor outlet temperature, 350 °C-550 °C. These are the noble metals with Pd as the most successful. The mid-temperature catalyst also has to be active, consisting preferably of metal oxides operating in the temperature range from 500 to 1000 °C and designed to withstand these high temperatures for long-time operation. The high-temperature catalyst has to be exceptionally stable, the surface reactions are very fast and the overall reaction rate is mass-transfer limited, therefore a large surface area might not be needed.
Therefore several different approaches have been proposed to limit the temperature of the catalyst surface as shown in fig. 5.2.

Figure 5.2 Different designs of catalytic combustion systems: (i) fully catalytic, (ii) secondary fuel, (iii) secondary air and (iv) passive channels [Thevenin 2002]

**Fully catalytic design (i)**

In the fully catalytic design different materials are used to fulfil different functions within the catalyst, hence the catalysts are segmented in the combustion chamber. The advantage of this design is that no secondary fuel or air is needed and the catalyst will work without any flame. The problem however is the very high temperatures needed in the last segment as discussed before. However fully catalytic combustors have been
suggested for recuperative gas turbines that utilise the exhaust gas to preheat the compressed air before entering the combustion chamber [Gabrielsson et al 1998], this solution could be viable for micro turbines using LHV fuels.

**Hybrid combustor with secondary fuel (ii)**

The hybrid combustor using secondary fuel is designed to lower the temperature in the catalyst segment by not allowing all of the fuel to pass over the catalyst, instead the secondary fuel is mixed in afterwards. The catalyst works as a kind of preheater to a temperature where ultra lean combustion may take place [Ozawa et al 1999].

**Hybrid combustor with secondary air (iii)**

The hybrid combustor using secondary air based on the RQL technique with a rich zone, has recently been proposed [Lyubovsky et al 2003]. In this design all fuel passes over the catalyst, however not enough air is present to fully oxidize the fuel within the limits of what the catalyst can withstand. Secondary air is mixed after the catalyst to fully oxidize all components in a homogeneous flame. The catalyst will both preheat the fuel, as in the hybrid combustor with secondary fuel, and “upgrade” the fuel by partial oxidation to more easily combustible components. This rich combustion technique could be successful for nitrogen-containing fuels like gasified waste, previously discussed in 4.2.2.

**Passive channels (iv)**

The passive channel approach has been designed and today commercialised by Catalytica Energy Systems [Kajita and Dalla Betta 2003]. The principle is the same as for the hybrid systems, to keep the catalyst temperature low. The fuel and air is mixed prior to the catalyst, however the fuel that passes over the uncoated passive channels remain uncombusted, resulting in lower temperatures over the catalyst. The hot fuel is then combusted in a post catalytic homogeneous zone after the catalyst to raise the temperature to the desired gas turbine inlet temperature.
**Commercial status: Catalytic combustion in gas turbines**

The development of catalytic combustor systems has recently been reviewed by Forzatti [2003]. He concludes that the most promising approach to catalytic combustion for gas turbines is based on the hybrid concept that relies on upstream fuel-air premixing with a two-stage combustion process. The first stage only oxidizes a fraction of the fuel and in the second stage downstream, the fuel is completely converted and the gases are heated to the desired combustor exit temperature. The catalytic combustion system best developed so far is the XONON cool combustion system by Catalytica Energy systems, which was released on the market in 2002. Average emissions of NO\textsubscript{x} <2.5 ppm, CO <6 ppm, and UHC <3 ppm at full load have been maintained for more than 8000 h. Other development activities are carried out by General Electric for the GE model MS9001E gas turbine, at Solar turbines for the Mercury 50 machines using a recuperative cycle, at Siemens Westinghouse Power corporation for a lean premixed combustor that incorporates a catalytic combustor and for a fully catalytic combustor, at Allison Engines, CRIEPI, Alstom Power, and Precision Combustion.

Forzatti [2003] concludes that catalytic combustion will first be applied into gas turbines with small or medium size, and with not too high firing temperature, this is also the kind of gas turbines suitable for LHV gases. For example Turbec is investigating how to employ catalytic combustion in their micro turbine T100, 100kW for biogas application.
6. CATALYTIC COMBUSTION OF GASIFIED WASTE

Catalysts for LHV gases (Paper I)

The development of novel materials for use in high-temperature catalytic combustion has continuously been carried out since the pioneering patent obtained by Pfefferle in 1975. The main research is, and has been, concentrated on methane as fuel, however a growing interest in environmental issues has opened the research into other fuels like LHV gases.

One of the main problems to overcome before implementing catalytic combustion in a gas turbine combustor is the ignition of the fuel at compressor outlet temperatures, especially for methane. Several concepts to achieve this have been proposed, some of them require engineering solutions with additional components such as preburners and electrical heaters. However, this adds to the complexity of the gas turbine and in the case of preburners is also a source of nitrogen oxide emissions. Hence, it would be preferable to have a catalyst with sufficient activity to ignite the fuel at the compressor outlet temperature - at least at full load. This means that the catalyst has to be active in the 350-550 °C temperature range depending on the type of gas turbine used. Noble metals are the most active catalysts for oxidation reactions [Gélin and Primet 2002]; for catalytic combustion the most successful is the Pd catalyst. It has been thoroughly investigated by many groups for the combustion of methane [Baker et al 1989, Farrauto et al 1992, Burch and Urbano 1995, McCarty 1995].

Using LHV gases as fuel in a gas turbine has a major advantage since it contains only a small amount of methane, the main combustible components are H₂ and CO, which both are considerably easier to ignite. However, LHV gas deriving from gasification of biomasses and wastes all contain fuel-bound nitrogen, which is difficult to prevent from forming NOₓ when using strong oxidizing catalysts to ignite the fuel. Therefore it
might be possible to use a stable metal oxide instead of noble metals as an ignition catalyst and at the same time reduce the formation of NO\textsubscript{X} following the idea suggested by Groppi et al [1998] and Johansson and Järås [1998].

Papers I and II report on the development and testing of novel catalysts for catalytic combustion of LHV gases. In paper I, suitable ignition catalysts and high-temperature materials are tested for LHV gases and in paper II pilot-scale tests are carried out to prove the potential to catalytically combust real gasified waste.

Several metal oxides have been proposed as combustion catalysts in the literature [Zwinkels et al 1993]. The substituted hexaaluminates, developed by Machida et al [1987], are among the most promising materials for catalytic combustion, due to their catalytic activity as well as their thermal stability. For the catalytic combustion of LHV gas, substituted hexaaluminates have proven to be a viable substitute for noble metals [Groppi et al 1998, Johansson et al 2002]. Especially the Mn-substituted hexaaluminate, \LaMnAl_{11}O_{19}, has shown high activity for combustion of LHV gas.

Spinels are another interesting group of materials with possible use as combustion catalysts. These materials have shown high thermal stability as well as promising activity in oxidation reactions [Marti et al 1994, Zwinkels et al 1998]. The spinel structure allows for several different substitutions of ions in a similar way as for the hexaaluminates, which could increase the catalytic activity. Thormählen et al [2001] have studied the oxidation of CO over a cobalt spinel for abatement of car exhaust emissions, in the presence of similar compounds as are found in LHV gases.

A third type of metal oxides with excellent high-temperature characteristics is garnets, or materials with garnet structure. Garnets have found a wide variety of applications ranging from laser crystals to magnetic materials and thermal barrier coatings. However, very few attempts to use garnets as catalytic materials have been reported in literature to this date [Haralambous et al 1991, Tsagaroyannis 1996]. The garnet structure also
allows for several different substitutions of ions that might improve the catalytic activity.

Paper I reports investigations on the use of spinel and hexaaluminate materials, both as active phase and impregnated with precious metals, as catalysts for the combustion of gasified RDF. The materials were tested with emphasis on the ignition characteristics of the main combustible components in the gasified waste, H₂, CO and CH₄, and compared to the combustion of pure methane. The conversion of NH₃ into N₂ and the formation of NOₓ were also studied over these catalysts.

The measurements of the catalytic activity of the catalysts were carried out in a tubular flow reactor equipped with a temperature-programmed furnace. In the experiments the temperature was increased by 5 °C/min from 100 to 900 °C and the space velocity corresponded to 100 000 h⁻¹. The tests were carried out using a synthetic gas mixture simulating gasified waste as shown in Table 3.1, with an air/fuel ratio equal to 3. To simulate the water content of the gasification gas water was added, pumped by a syringe pump and evaporated prior to the reactor inlet and mixed with air in the preheating zone of the reactor, as seen in fig 6.1.

Figure 6.1 Lab-scale reactor
The on-line gas analysis methods used for the flue gas emission measurement are shown in Table 6.1.

<table>
<thead>
<tr>
<th>Gas compound</th>
<th>Measurement principle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>NDIR</td>
</tr>
<tr>
<td>CO</td>
<td>NDIR</td>
</tr>
<tr>
<td>CO₂</td>
<td>NDIR</td>
</tr>
<tr>
<td>NH₃</td>
<td>NDIR</td>
</tr>
<tr>
<td>NO</td>
<td>NDIR</td>
</tr>
<tr>
<td>NO₂</td>
<td>UV</td>
</tr>
<tr>
<td>O₂</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>H₂</td>
<td>Thermal conductivity</td>
</tr>
</tbody>
</table>

In paper I it is confirmed that the noble metals Pd and Pt impregnated on different washcoat materials easily ignite the fuel components H₂ and CO, already at 200 °C for the Pd catalyst, see fig 6.2 and at about 100 °C higher for the Pt catalyst; both are at temperatures well below the compressor outlet temperature. NH₃ was added to the fuel to simulate fuel-bound nitrogen, in order to evaluate the formation of fuel NOₓ over the catalysts. At light-off both the Pd and Pt catalysts convert almost all NH₃ into NOₓ, which corresponds well with the fact that Pt catalysts are used for nitric acid production [Kroschwitz 1996].
As expected the Mn-substituted hexaaluminate showed high activity for combustion of LHV gas for all fuel components both as active phase and impregnated with Pd. In the experimental series reported in paper I the idea was to integrate the active manganese atom into the spinel structure to improve the activity of the spinel catalyst. The Mn-substituted spinel showed good activities for H$_2$ and CO, well comparable to those of LaMnAl$_{11}$O$_{19}$. However, incorporating manganese atoms in the spinel lattice did not enhance the catalytic activity for the methane component in the LHV gas as it did for the hexaaluminates. The spinel materials show high thermal stability and can preferably be used as washcoat material avoiding sintering at high temperatures.

Two types of garnet catalyst materials, i.e. Y$_3$Al$_5$O$_{12}$, and a Mn-substituted garnet, Y$_3$Mn$_{0.1}$Al$_{4.9}$O$_{12}$, have also been prepared and tested in lab scale under similar conditions as described above [Ersson 2003b]. The Y$_3$Al$_5$O$_{12}$ catalyst is shown in figure 6.3, a rapid increase in conversion of H$_2$ and CO occurs at around 450 °C. The activity of the Y$_3$Al$_5$O$_{12}$ is higher than the previously studied Mn-substituted hexaaluminate.
Substitution of manganese into the crystal lattice of Y$_3$Al$_5$O$_{12}$ did not improve the catalytic activity for LHV gas combustion, instead the activity decreased for the fuel components H$_2$ and CO. The Y$_3$Al$_5$O$_{12}$ showed 50 % N$_2$ selectivity at temperatures between 470 °C and 560 °C; in this temperature window the conversion of NH$_3$ remained constant at 50 %, as the temperature increases the N$_2$ selectivity drops to a minimum of 20 % at 700 °C.

The metal oxide catalysts showed lower NO$_X$ yields than the noble metal-based catalysts, but are not satisfactory. Lietti et al [1999] suggested that, at high temperatures, homogeneous reactions start to take over, reducing the NO$_X$ formed down by 50-60 %. In paper I homogeneous reactions were observed at temperatures above 770 °C for the hexaaluminates and the spinels and at around 750 °C for the garnets. The non-catalytic nature of the reaction was confirmed by combustion over an uncoated cordierite, showing a similar decrease in NO$_X$ formation as over the catalysts. This clearly shows the problem with designing a catalytic combustion system that can selectively oxidize NH$_3$ to N$_2$ and still achieve high conversions of the fuel components.
Pilot-scale testing (Paper II)

Normally when testing catalysts the experiments are carried out in laboratory scale with a synthetic gas mixture simulating the gasified fuel. Therefore catalytic combustion experiments with real gasified waste like RDF are important, not only for the studying of the catalyst behaviour and its resistance towards deactivation and possible fuel-NOx formation, but also to understand and control the gasification process. Such tests with real LHV gas have previously been carried out with gasified pelletized sawdust [Berg et al 2000]. However like for biomasses, the composition of waste material varies, the main components of the gas are alike, but the fuel composition of the feed gas depends also on the gasification technique and gas cleaning systems and not only on the raw material.

In paper II, real gasified waste was tested and compared with a synthetic gas over the most active catalysts reported for high-temperature catalytic combustion, i.e. Mn-substituted hexaaluminates with/without Pd impregnation. The pilot-scale testing was performed in a combustion rig connected to a pilot unit gasifier at TPS AB, see fig. 6.4.  

Figure 6.4 Pilot-scale equipment, at left the gasification unit and at right the catalytic combustion unit [Berg et al 1998]

The gasification unit is an atmospheric fluidized bubble-bed gasifier designed for biomass-derived fuels. The feeding system to the gasifier is pressurized with nitrogen. Both the primary air to the gasifier and the gasifier are electrically heated in order to minimise heat losses. Gas
corresponding to 20-30 kW can be produced. Downstream the gasifier particles are separated from the gas by a cyclone and a ceramic filter, which operates at around 400 °C. The produced gas is then led to a mixing chamber where the gas is mixed with the air and then enters the catalytic combustion unit.

The catalytic combustion unit basically consists of a two meter long insulated pipe with two pre-heated air inlets connected at the beginning of the pipe, and a holder for the catalysts segments at the end. Both the magnitude of preheating and the flow of air may be altered at any time to obtain the wanted temperature and air/fuel ratio. Three thermocouples were used to measure the temperature in the catalyst. When a single catalyst was used under testing, the thermocouples were placed in different positions, both radially and axially. When multiple segments were used the thermocouples were placed in the different segments. The space velocity was changed throughout the tests. The airflow was changed from 50 to 70 Nm³/h, resulting in a space velocity of 750 000 h⁻¹ calculated over one catalyst segment at an airflow of 70 Nm³/h. The fuel-gas flow from the gasifier contributed with an additional space velocity of 150 000 h⁻¹. The design of the combustion rig enabled the catalyst to be inspected visually during the tests to conclude whether the combustion was uniform throughout the radius or not.

The waste material was successfully gasified producing a stable low heating-value gas. The waste containing high amounts of ashes, 16 %, did not affect the gasification process nor did it affect the product gas. The Pd/LaMnAl₁₁O₁₉ catalyst showed high activity for the real gasified RDF in the pilot-scale experiments. The LaMnAl₁₁O₁₉ was also placed as a light-off catalyst in the first segment, but was not able to ignite the fuel gas during the test; the combustion activity of the material was not high enough. When the temperature was elevated to temperatures around 400 °C in the mixing point, the gas auto-ignited in the mixing section before the catalyst. At low temperatures LaMnAl₁₁O₁₉ was probably deactivated due to sulfur poisoning as reported in paper V. However, the Pd catalyst did not show significant signs of deactivation, the light-off temperature was about 100 °C higher in the pilot-scale experiments indicating possible poisoning, but
Overall the results were satisfying since earlier studies reported sulfur deactivation of both the Pd catalyst and the metal oxide, LaMnAl$_{11}$O$_{19}$ [Berg et al 2000].

Placed as second and third segments, the LaMnAl$_{11}$O$_{19}$ was active above 700 °C even with the presence of sulfur in the feed; then Pd/LaMnAl$_{11}$O$_{19}$ was placed as the first segment igniting the fuel, see figure 6.5.

![Figure 6.5. Light-off temperature and temperature profiles at different airflows over the different catalyst segments](image)

The conversion of CO and THC increased with extra catalyst layers of LaMnAl$_{11}$O$_{19}$. However three segments were not enough to completely convert the fuel components.

The NO$_X$ formation in the pilot-scale experiments did not show any significant difference between the tests. Despite the expected higher degree of formation in the test with multiple segments, all tests showed a similar formation of NO$_X$. All NO$_X$ was hence formed over the first light-off segment, Pd/LaMnAl$_{11}$O$_{19}$. However, the fuel-NO$_X$ formation was high under all catalyst configurations ranging from 55 % to 90 % yield with the
highest NO\textsubscript{X} formation for the configurations with the highest fuel conversions.

As seen in paper I, these kinds of highly oxidizing catalysts are not the best as NO\textsubscript{X} reducing catalysts, but are good for the light-off and maintenance of the fuel conversion. Therefore unless a selective NH\textsubscript{3} oxidation catalyst is used before the total oxidation of the fuel components this kind of LHV gases needs the use of an appropriate exhaust gases cleaning system. In paper III, a selective catalytic oxidation process for decreasing the NO\textsubscript{X} formation from fuel-bound nitrogen is investigated.

**Circumventing NO\textsubscript{X} (Paper III)**

As could be concluded in papers I and II, the NO\textsubscript{X} formation is too high over the tested active oxidizing catalysts. The group of Burch have proposed different selective catalytic oxidation processes for decreasing the NO\textsubscript{X} formation from fuel-bound nitrogen. Under fuel-lean conditions they were successful with N\textsubscript{2} yields above 90\% \[\text{Amblard et al 1999}\] on Ni, Fe and Mn catalysts supported on $\gamma$-Al\textsubscript{2}O\textsubscript{3}, however, with limited operating temperature ranges. Another approach was made \[\text{Burch and Southward 2000c}\] by taking advantage of a different mechanism, namely the coupled NH\textsubscript{3} oxidation/CO/H\textsubscript{2}-NO\textsubscript{X} reduction process. The important feature was to limit the O\textsubscript{2} using process control with a highly selective catalyst, using lean/rich switches to first oxidize all the ammonia to NO\textsubscript{X} and then utilize the large excess of CO and H\textsubscript{2} in the gas stream to reduce the NO\textsubscript{X} to N\textsubscript{2} through NO/CO and NO/H\textsubscript{2} reactions. They further presented \[\text{Burch and Southward 1999}\] a fuel-rich concept with a catalyst, H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}, containing acid sites to differentiate ammonia from CO and H\textsubscript{2}, and redox properties to oxidize the adsorbed species, achieving almost no NO\textsubscript{X} formation above 600 °C. Table 6.2 presents an overview of promising catalysts for selective catalytic oxidation of NH\textsubscript{3} to N\textsubscript{2} that have been investigated in the literature, and tested under different gas compositions and conditions, all showing high N\textsubscript{2} yields.
<table>
<thead>
<tr>
<th>Catalyst composition</th>
<th>Composition of testing gas</th>
<th>Conditions</th>
<th>Temp (°C)</th>
<th>N₂ yield (%)</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃PW₁₂O₴₀</td>
<td>1050 ppm NH₃, 0.5% O₂, 6% CO, 4% H₂</td>
<td>SV=250 000 h⁻¹</td>
<td>600</td>
<td>85</td>
<td>tested with rich mixture</td>
<td>[Burch&amp;Southward 1999]</td>
</tr>
<tr>
<td>1% Pt 20% CuO/Al₂O₃</td>
<td>1000 ppm NH₃, 2.1% O₂, 1.02% CO, 0.68% H₂</td>
<td>SV=240 000 h⁻¹</td>
<td>200</td>
<td>94</td>
<td>lean/rich switches tested</td>
<td>[Burch&amp;Southward 2000a]</td>
</tr>
<tr>
<td>1% Pt 20% CuO/Al₂O₃</td>
<td>1000 ppm NH₃, 9.3% O₂, 5.1% CO, 3.4% H₂</td>
<td>SV=240 000 h⁻¹</td>
<td>200</td>
<td>15</td>
<td>lean/rich switches tested</td>
<td>[Burch&amp;Southward 2000b]</td>
</tr>
<tr>
<td>2% Rh/Al₂O₃</td>
<td>1000 ppm NH₃, 18% O₂</td>
<td>SV=240 000 h⁻¹</td>
<td>375</td>
<td>63</td>
<td>second test under rich conditions</td>
<td>[Burch&amp;Southward 2000c]</td>
</tr>
<tr>
<td>1% Pt 20% CuO/Al₂O₃</td>
<td>1000 ppm NH₃, 2.05% O₂, 1.02% CO, 0.68% H₂</td>
<td>SV=240 000 h⁻¹</td>
<td>200</td>
<td>87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Pt 20% BaO/Al₂O₃</td>
<td>1000 ppm NH₃, 0.275% O₂, 1.02% CO, 0.68% H₂</td>
<td>SV=240 000 h⁻¹</td>
<td>625</td>
<td>= 100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% Pt 20% CuO/Al₂O₃</td>
<td>1000 ppm NH₃, 18% O₂</td>
<td>SV=240 000 h⁻¹</td>
<td>300</td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Ni/Al₂O₃</td>
<td>1000 ppm NH₃, 18% O₂</td>
<td>SV=6 000 h⁻¹</td>
<td>550</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Mn/Al₂O₃</td>
<td>1000 ppm NH₃, 18% O₂</td>
<td>SV=6 000 h⁻¹</td>
<td>300</td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Fe/Al₂O₃</td>
<td>1000 ppm NH₃, 18% O₂</td>
<td>SV=6 000 h⁻¹</td>
<td>500</td>
<td>94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Fe₂O₃/TiO₂(SO₄²⁻)</td>
<td>1000 ppm NH₃, 10% O₂</td>
<td>100 cm³/min, 0.1 g *c.</td>
<td>160</td>
<td>82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Fe₂O₃/TiO₂(SO₄²⁻)</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=200 000 h⁻¹</td>
<td>450</td>
<td>94</td>
<td>N₂ yield decreases slightly in the presence of water</td>
<td>[Long&amp;Yang 2002]</td>
</tr>
<tr>
<td>21% MoO₃/SiO₂</td>
<td>960 ppm NH₃, 9000 ppm O₂, 1500 ppm Ar</td>
<td>SV=200 000 h⁻¹</td>
<td>625</td>
<td>= 100</td>
<td>N₂ selectivity decreases with decreasing ammonia conc., water strongly reduces reactivity of catalysts</td>
<td>[Lietti et al 2000]</td>
</tr>
<tr>
<td>Bi-doped 16% MoO₃/SiO₂</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=200 000 h⁻¹</td>
<td>300</td>
<td>90</td>
<td>influence of water in feed also tested</td>
<td>[Li&amp;Armor 1997]</td>
</tr>
<tr>
<td>4.1% Pd-ZSM-5</td>
<td>1000 ppm NH₃, 4% O₂</td>
<td>100 cm³/min, 0.1 g *c.</td>
<td>300</td>
<td>79</td>
<td>Pd-ZSM-5 is recommended for wet atmosphere</td>
<td></td>
</tr>
<tr>
<td>4.2% PdO/Al₂O₃</td>
<td>1000 ppm NH₃, 4% O₂</td>
<td>100 cm³/min, 0.1 g *c.</td>
<td>270</td>
<td>87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.2% PdO/Al₂O₃ reduced</td>
<td>1000 ppm NH₃, 4% O₂</td>
<td>100 cm³/min, 0.1 g *c.</td>
<td>250</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.6% Rh-Na-ZSM-5</td>
<td>1000 ppm NH₃, 4% O₂</td>
<td>100 cm³/min, 0.1 g *c.</td>
<td>275</td>
<td>96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.13% Cr-ZSM-5(10)</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=230 000 h⁻¹</td>
<td>450</td>
<td>90</td>
<td>conversion of NH₃ decreased slightly by water,</td>
<td>[Long&amp;Yang 2000]</td>
</tr>
<tr>
<td>1.59% Fe-ZSM-5(10)</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=230 000 h⁻¹</td>
<td>450</td>
<td>99</td>
<td>significantly by SO₂ and SO₂ + H₂O on Fe-ZSM-5</td>
<td></td>
</tr>
<tr>
<td>0.85% Cu-ZSM-5(10)</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=230 000 h⁻¹</td>
<td>450</td>
<td>97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6% Fe(58)-ZSM-5(10)</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=230 000 h⁻¹</td>
<td>450</td>
<td>99</td>
<td>high iron content, low Si/Al ratio, low ammonia concentration and low space velocity</td>
<td>[Long&amp;Yang 2001a]</td>
</tr>
<tr>
<td>2.4% Fe(60)-MOR(6,4)</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=230 000 h⁻¹</td>
<td>450</td>
<td>97</td>
<td>are favourable</td>
<td></td>
</tr>
<tr>
<td>3.5% Fe(81)-HEU(5)</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=230 000 h⁻¹</td>
<td>450</td>
<td>98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt-doped Fe-ZSM-5</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=230 000 h⁻¹</td>
<td>250</td>
<td>91</td>
<td>water and SO₂ decrease the N₂ yield only slightly</td>
<td>[Long&amp;Yang 2001b]</td>
</tr>
<tr>
<td>Ce-doped Fe-ZSM-5</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=230 000 h⁻¹</td>
<td>400</td>
<td>91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd-doped Fe-ZSM-5</td>
<td>1000 ppm NH₃, 2% O₂</td>
<td>SV=230 000 h⁻¹</td>
<td>400</td>
<td>89</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*c. = catalyst
In paper III we followed the idea to selectively oxidize NH$_3$ using two different approaches: fuel-lean and fuel-rich conditions using a LHV gas over the following catalysts; 5%Fe/Al$_2$O$_3$, 5%Mn/Al$_2$O$_3$, 20%CuO/Al$_2$O$_3$, 1%Pt/20%CuO/Al$_2$O$_3$, 2%Rh/Al$_2$O$_3$ and a Fe zeolite (Fe-SH-27). The fuel-lean concept for catalytic combustion is supposed to be placed as a first segment inside the combustion chamber and could be implemented in any of the proposed reactors described in section 5.3. For the fuel-rich concept the catalyst could be placed somewhere before the gas turbine and directly after the filter and cleaning of the product gas from the gasifier.

The selective catalytic oxidation performances of the catalysts were examined in the same reactor described earlier for the lab-scale experiments. As mentioned the catalysts were tested in both fuel-lean conditions ($\lambda$=3) and in fuel-rich conditions ($\lambda$=0.2) using a LHV gas. Additionally, water was added in some experiments. The experimental temperature regime was chosen to be equal to the compressor outlet temperature of a gas turbine and the steady state behaviour of the catalysts was tested in the range from 250 °C to 500 °C with steps of 50 °C for 30 min or in chosen ranges with steps of 20 °C for 60 min.

For the fuel-lean conditions, the Fe zeolite catalyst showed promisingly low NO$_X$ yields, using a dry LHV gas, however, water added to the stream increased the selectivity for NO$_X$ formation to NO$_X$ yields slightly below 50%, just as previously reported [Amblard et al 1999].

For fuel-rich conditions the CuO/Al$_2$O$_3$ catalyst showed extremely low NO$_X$ selectivities, only 1ppm could be detected. This was also obtained with water added to the LHV gas stream over a wide temperature range, 300-500 °C, see Table 6.3.
Table 6.3 The CuO/Al₂O₃ performance under fuel-rich conditions; set values: \( \lambda = 0.2 \), \( SV = 100,000 \, h^{-1} \), duration at each temperature = 60 min.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Temperature (°C)</th>
<th>NH₃ conversion (%)</th>
<th>Selectivity (%)</th>
<th>NOₓ yield (%)</th>
<th>N₂ yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>furnace setting</td>
<td>cat. inlet</td>
<td>NO</td>
<td>NO₂</td>
<td></td>
</tr>
<tr>
<td>CuO - dry</td>
<td>300</td>
<td>279</td>
<td>75</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>301</td>
<td>70</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>324</td>
<td>71</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>348</td>
<td>75</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>371</td>
<td>79</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>393</td>
<td>81</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>416</td>
<td>82</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>440</td>
<td>439</td>
<td>81</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>460</td>
<td>461</td>
<td>81</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>480</td>
<td>483</td>
<td>80</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>506</td>
<td>79</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>CuO with 3.9% H₂O</td>
<td>300</td>
<td>302</td>
<td>50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>323</td>
<td>54</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>344</td>
<td>61</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>366</td>
<td>63</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>388</td>
<td>64</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>408</td>
<td>65</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>430</td>
<td>66</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>440</td>
<td>451</td>
<td>67</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>460</td>
<td>472</td>
<td>69</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>480</td>
<td>493</td>
<td>68</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>514</td>
<td>68</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

From the results obtained in paper III, the fuel-rich approach appears to be the most promising way to selectively oxidize NH₃ to N₂ and would also be the most simple way to clean the gas stream from NH₃ that might form NOₓ inside the gas turbine. The CuO/Al₂O₃ catalyst has to be tested further as to poisoning by sulfur and other possible poisons to the catalyst. In the next chapter the deactivation of catalysts is discussed, including the poisoning by sulfur over the metal oxide catalysts tested in paper I.
7. DEACTIVATION (PAPERS IV AND V)

When developing a catalyst, there are many aspects that have to be taken into account; first the catalyst should be active for the desired reaction, it should be as selective as possible avoiding unnecessary formation of by-products. Of major importance is the life-time of a catalyst, all catalysts deactivate sooner or later, even though the definition of a catalyst is that it is not consumed or destroyed during the reaction. For some chemical processes the deactivation of the catalyst can be very fast, however the catalyst might still be successful if it is relatively inexpensive and easy to replace or regenerate.

A successful combustion catalyst has to fulfil several criteria. First the ignition has to occur at the compressor outlet temperature and the activity has to be high enough to maintain complete combustion at the lowest temperature and the highest value of mass throughput from the compressor. Moreover, the substrate should have a large geometric surface area, low pressure drop, good thermal shock resistance, and it should allow high working temperatures. The washcoat should maintain its surface area at combustion conditions.

The catalyst in a gas turbine combustor must at least withstand 8000 hours [Carroni et al 2002], i.e. approximately one year of continuous operation in an environment that is extremely harsh, with high temperature and pressure, high gas velocities, and high concentrations of steam. Using gasified waste as fuel even increases the possibilities of deactivation compared to natural gas, which is a much cleaner fuel. The product gas from the gasifier contains many possible poisons to the catalyst, like alkali metals, chlorine and sulfur compounds, and therefore gas filtration plays a key role in almost all applications of biomass or waste gasification, even very small concentrations might be enough to poison the catalyst.

Paper IV focuses on sintering, material vaporization, phase transformation, thermal shock, and poisoning, as they are the most important forms of deactivation in high-temperature catalytic combustion with natural gas or methane as the fuel. All these deactivation phenomena are essential in
catalytic combustion, however poisoning will be of even more significance using gasified waste instead of methane; this is further discussed in paper V.

**Deactivation of combustion catalysts (Paper IV)**

The objective of paper IV was to review and discuss the different phenomena of deactivation for a catalytic system present in a gas turbine combustor. The deactivation of combustion catalysts has been reviewed by several authors [Trimm 1997, Forzatti and Lietti 1999, McCarty et al 1999]. There are many ways in which a catalyst can deactivate. The catalyst deactivation can be divided into four main categories, poisoning, sintering, coking or fouling, and phase transformation. There are also other mechanisms that can cause deactivation of the catalyst: attrition, material volatilisation and erosion. Fouling or coking is not a big issue in high-temperature catalytic combustion, because of the high temperatures. Regardless of the kind of fuel, sintering, vaporization, phase transformation and thermal shock are deactivation phenomena that will be present in the gas turbine environment.

**Sintering**

Sintering is one of the most important causes for loss of surface area of combustion catalysts [McCarty et al 1999]. Sintering is usually a physical process and is thermally activated. The combination of very high temperatures and steam causes severe sintering and loss of surface area for most of the common catalyst materials. Therefore much effort has been spent on finding materials with high resistance to sintering, which can affect the active component as well as the support.

For supported metal catalysts, two different models for sintering have been proposed, atomic migration and crystallite migration [Forzatti et al 1999]. According to the first, sintering occurs due to metal atoms migrating from one crystallite to another via the surface or the gas phase. The crystallite size will therefore increase, yielding a lower surface area. According to the second model, sintering occurs via crystallite migration over the surface followed by collision and coalescence of the crystallites.
In catalytic combustion, metal oxides are generally less active than supported precious metals, but more resistant to sintering and less volatile. The sintering due to particle migration is not as pronounced for metal oxides as for supported metals. The sintering is primarily limited by diffusion of metal cations between two neighbouring particles. Anion diffusion is rarely limiting due to the presence of oxygen and steam in the combustion atmosphere. During the sintering process, the pore size and/or shape are changed [Kingery et al 1976], usually simultaneously.

The low sintering resistance excludes most single metal oxides from use as washcoat in catalytic combustion. Therefore the interest has been diverted towards complex metal oxides, like hexaaluminates, spinels and garnets, which all have high surface areas at these severe temperatures. Furthermore different preparation techniques influence the thermal stability of the catalyst [Ersson et al 1998].

**Vaporization**

When the material is heated above a critical temperature, the vapour pressure of the metal or the metal oxide rises so that significant amounts of material can be transported either to react with the substrate or are lost in the effluent gas stream. Vaporization can also cause the migration of other components (corrosive components, contaminants) that may accumulate on the surface and block catalytically active sites. In high-temperature catalytic combustion vaporization is an important factor. Pd is the most suitable noble metal with respect to vaporization followed by Ir, Pt, and Ru in order of increasing volatility [Hildenbrand et al 1992].

**Phase transformation**

The high temperature involved in catalytic combustion may cause migration of atoms within the crystal lattice of the catalyst materials. This could give rise to sintering of the catalysts. If the catalyst is built up of two or more different materials diffusing atoms can react with the neighbouring materials, giving rise to severe deactivation of the catalyst.

**Thermal shock**

During the start-up of the combustion process the monolith temperature increases rapidly. The process changes often cause sudden temperature
increases or decreases within the monolith, possibly hundreds of degrees per second, resulting in thermal stress [Trimm 1995]. The walls of the monolith will cool faster than the bulk and this gives a thermal gradient within the ceramic, leading to fractures [Wright et al 1983, Lox and Engler 1999]. When the washcoat and the catalyst substrate, that usually have different thermal expansion coefficients, are subjected to thermal cycling, the result is stress in the coating and it will lead to cracks [Morrel 1985]. In Table 7.1 high temperature materials for catalytic combustion are shown.

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Maximum Temperature [ºC]</th>
<th>Thermal expansion 10^-6 [cm/ºC]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium titanate</td>
<td>Al₂TiO₅</td>
<td>1800</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Corderite</td>
<td>Mg₂Al₃Si₅O₁₈</td>
<td>1200-1400</td>
<td>1</td>
<td>Excellent thermal shock resistance</td>
</tr>
<tr>
<td>Dense alumina</td>
<td>α-, γ-Al₂O₃</td>
<td>1500-1600</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>FeCr alloy</td>
<td>15%Cr, 5% Al, Y traces, balance Fe</td>
<td>1250-1350</td>
<td>11</td>
<td>Excellent thermal shock resistance</td>
</tr>
<tr>
<td>Magnesia</td>
<td>MgO</td>
<td>1800</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Mullite</td>
<td>Al₆Si₂O₁₃</td>
<td>1350</td>
<td>2</td>
<td>Good corrosion resistance</td>
</tr>
<tr>
<td>Mullite aluminium titanate</td>
<td>-</td>
<td>1550</td>
<td>4</td>
<td>Good thermal shock</td>
</tr>
<tr>
<td>NZP</td>
<td>NaZr₂(PO₄)₃</td>
<td>&lt;1500</td>
<td>&lt;2</td>
<td></td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>SiC</td>
<td>1550-1650</td>
<td>5</td>
<td>Good thermal shock resistance</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>Si₃N₄</td>
<td>1200-1540</td>
<td>3.7</td>
<td>Good thermal shock resistance</td>
</tr>
<tr>
<td>Spinel</td>
<td>MgAl₂O₄</td>
<td>1400</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>YAG</td>
<td>Y₃Al₅O₁₂</td>
<td>&gt;1400</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>Zirconia</td>
<td>ZrO₂</td>
<td>2200</td>
<td>10</td>
<td>Good thermal shock resistance</td>
</tr>
<tr>
<td>Zirconia-spinel</td>
<td>-</td>
<td>1700</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Zirconium mullite</td>
<td>-</td>
<td>1550</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

Poisoning (Papers IV and V)

In catalytic combustion, even a slow poisoning or traces of poisons may cause sufficient deactivation of the catalyst to impede any commercial application. The poisoning may be reversible or irreversible. If the
poisoning is reversible the catalytic activity is restored once the poison has been removed through some generating procedure.

In waste material, as well as in gasified biomass, sulfur is present and could be a potential catalyst poison, even in small concentrations [Lee et al 1995, Lampert et al 1997, Johansson et al 1999]. The sulfur in gasified biomass is present mainly as H\textsubscript{2}S and to some extent COS. Gasification studies have shown that gasified industrial waste has similar sulfur contents as typical biomass even though concentration varies depending on the type of waste. Typical levels for gasified biomass is between 20 and 200 ppm [Berg et al 1997]. The retention of sulfur on the surface of the catalyst occurs through the formation of surface sulfates [Shelef et al 1978]. H\textsubscript{2}S is directly oxidized into SO\textsubscript{2} or SO\textsubscript{3} that reacts further with the metal oxide to form metal sulfate. Depending on the support material it could also greatly influence the poisoning effect [Hoyos et al 1993].

The objective of paper V was to study catalytic combustion and the poisoning effect of low amounts of sulfur in the catalytic combustion of gasified waste over palladium and platinum catalysts on various support materials, i.e. hexaaluminates, spinel and garnets.

The catalytic activity of the monolithic catalysts was measured using a tubular flow reactor equipped with a furnace that allows the temperature to be ramped between room temperature and 1000 °C with 3 °C/min, similar to the one described earlier in chapter 6. The tests were carried out using LHV gas in single run tests. The reaction products were measured with an on-line GC. The fresh catalysts were first tested for activity in combustion of the synthetic gasified waste, and then the test was repeated with an addition of 25 ppm sulfur dioxide to the gas mixture.

The fresh Pd-impregnated catalysts showed the best conversion of all LHV-fuel components (H\textsubscript{2}, CO, CH\textsubscript{4}), on all the different support materials, however the poisoning affected the catalysts differently depending on the type of active component. The Pt catalysts showed almost no deactivation while the Pd catalysts became severely deactivated for CH\textsubscript{4}, while the H\textsubscript{2} and CO combustion remained the same.
The metal oxide-based catalysts, i.e. the un-impregnated washcoats, also form metal sulfates and sulfites with SO₂ [Khairulin et al 1997, Rosso et al 2001]. These compounds are generally less stable at the high temperature which is required for CH₄ combustion, and hence they were not affected by the SO₂. For H₂ and CO their ignition temperatures are well within the stability range for the metal sulfates, and their conversion decreased. The hexaaluminate LaMnAl₁₁O₁₉ and the spinel MgAl₂O₄ were both severely deactivated in the presence of sulfur, while the garnet, Y₃Al₅O₁₂, showed an improvement of the activity with an addition of SO₂; this could probably be attributed to the increased acidity of the catalysts, as has been described for alumina catalysts [Hoyos et al 1993, Hosoya and Shimoda 1996, Meeyoo et al 1998], see fig. 7.1.

![Figure 7.1](image_url)  

**Figure 7.1 Sulfur poisoning of the Y₃Al₅O₁₂ catalyst**

Hence the garnet material might be very interesting for use as washcoat material for gas streams containing small amounts of SO₂ like gasified waste. The light-off of H₂ and CO are, as shown earlier, better than for the LaMnAl₁₁O₁₉, which however is superior for the CH₄ component.
8. CONCLUSIONS

Catalytic combustion of natural gas has been investigated by numerous research groups both at universities and for commercial purposes, as it offers high efficiency combustion at extremely low emission levels. Single digit ppm emission levels of carbon monoxide, hydrocarbons and nitrogen oxides have been demonstrated in various pilot-scale experiments and the technique has recently been commercialised. The development of catalytic combustion systems for LHV gas will certainly profit from the improved understanding of the physical and chemical processes involved in the combustion of natural gas. The overall objective of this thesis was to investigate the feasibility of catalytic combustion for gas turbine application using a LHV gas, derived from gasified waste. The thesis shows that it is possible to catalytically combust a LHV gas and to reduce fuel-bound nitrogen (NH₃) directly into N₂ without forming NOₓ.

In Paper I the idea was to use a stable metal oxide instead of noble metals as ignition catalyst and at the same time reduce the formation of NOₓ. It was confirmed that the noble metals Pd and Pt impregnated on the different washcoat materials easily ignite the fuel components H₂ and CO, at pleasingly low temperatures, however they also converted almost all NH₃ into NOₓ. The metal oxide catalysts showed relatively good activity towards the fuel components in the LHV gas, but were not as active as the noble metals. The metal oxides showed lower NOₓ yields, but still 50-60% NOₓ yield was formed.

In paper II real gasified waste was tested and compared with a synthetic gas over the most active catalysts reported for high-temperature catalytic combustion, i.e. Mn-substituted hexaaluminates with/without Pd impregnation. The Pd/LaMnAl₁₁O₁₉ catalyst showed high activity for the real gasified waste in the pilot-scale experiments. The metal oxide, LaMnAl₁₁O₁₉, was also placed as ignition catalyst in the first segment, but was not able to ignite the fuel gas during the test; the combustion activity of the material was not high enough. When the temperature was elevated to
around 400 °C in the mixing point, the fuel auto-ignited in the mixing section before the catalyst. At low temperatures LaMnAl$_{11}$O$_{19}$ was probably deactivated due to sulfur poisoning, as reported in paper V. However, the Pd catalyst did not show significant signs of deactivation though the light-off temperature was about 100 °C higher in the pilot-scale experiments, indicating possible poisoning, but overall the results were satisfying since earlier studies reported sulfur deactivation of both the Pd catalyst and the metal oxide, LaMnAl$_{11}$O$_{19}$.

Still, the fuel-NO$_X$ formation was high during the pilot-scale experiments ranging from 55 % to 90 % NO$_X$ yield. As concluded in both papers I and II, these kinds of highly oxidizing catalysts are not the best as NO$_X$ reducing catalysts, but are good for the light-off and maintenance of the fuel conversion. Therefore a selective NH$_3$ oxidation catalyst is needed before the total oxidation of the fuel components takes place, otherwise this kind of LHV gases needs the use of an appropriate exhaust gas cleaning system.

The results obtained in paper III, where the idea was to selectively oxidize NH$_3$ into N$_2$ under both fuel-lean and fuel-rich conditions showed that the fuel-rich approach appears to be the most promising way. The fuel rich approach would be the easiest way to clean the gas stream from NH$_3$ that might form NO$_X$ inside the gas turbine. The CuO/Al$_2$O$_3$ catalyst showed extremely low NO$_X$ selectivities, only 1ppm could be detected. This was also obtained under realistic conditions with water added to the LHV gas stream over a wide temperature range, 300-500 °C.

In paper V the deactivation due to sulfur poisoning was studied on various metal oxides as well as on supported palladium and platinum catalysts. Among the noble metal-based catalysts the Pd-impregnated catalysts showed the best conversion of all LHV-fuel components, on all the different washcoat materials; however, an addition of 25 ppm SO$_2$ to the gas stream severely deactivated the Pd catalysts for CH$_4$, while the H$_2$ and CO combustion remained the same, while the Pt catalysts showed almost no deactivation.
For the metal oxide-based catalysts, i.e. the un-impregnated washcoats, the hexaaluminate LaMnAl$_{11}$O$_{19}$ and the spinel MgAl$_2$O$_4$ were both severely deactivated in the presence of sulfur, while a garnet, Y$_3$Al$_5$O$_{12}$, showed an improvement of the activity with an addition of SO$_2$. This makes the garnet, Y$_3$Al$_5$O$_{12}$, very interesting for use as washcoat material for gas streams containing small amounts of SO$_2$ like gasified waste. The light-off of H$_2$ and CO are better for the garnet than for the LaMnAl$_{11}$O$_{19}$, which however is superior for the CH$_4$ component, but such high activity for the methane component is probably not needed for the light-off of a LHV gas.

I believe that with the results obtained in this thesis it would be possible to compose a working catalytic system for gas turbine application using a LHV gas. For this probably a smaller recuperative gas turbine is the most viable. The NH$_3$ in the gasified waste or biomass would first be selectively oxidized to N$_2$ using the fuel-rich concept with the CuO/Al$_2$O$_3$ catalyst. The catalyst may be placed before the gas turbine somewhere after the filter and cleaning of the product gas from the gasifier. The LHV gas, now clean from NH$_3$, could be ignited by a noble metal catalyst, preferably Pt since it is not deactivated by the sulfur that will be present in the stream and Pt has a light-off temperature well below the compressor outlet temperature or the Pd catalyst since it was also shown that it can ignite H$_2$ and CO even in the presence of sulfur. As washcoat material the garnet, Y$_3$Al$_5$O$_{12}$, would be chosen, since it actually increased its activity with sulfur present in the stream. As mid-temperature catalyst the Mn-substituted hexaaluminate, LaMnAl$_{11}$O$_{19}$, would be chosen since it has good activity for the combustion of the methane component in the fuel and does not seem to be poisoned by sulfur at temperatures above 650 °C, where the sulfates/sulfites no longer are stable on the surface.

However before implementation the CuO/Al$_2$O$_3$ catalyst has to be tested further towards poisoning by sulfur as well as other possible poisons to the catalyst.
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REFERENCES


My contributions to the papers

**Paper I** (Co-authors: Ersson A.G., Järås S.G.)
In this paper I carried out most of the laboratory experiments and was responsible for writing the paper together with Anders Ersson. The paper was revised by all of the authors.

**Paper II** (Co-authors: Ersson, A.G., Elm Svensson E., Järås, S.G.)
In this paper I carried out some laboratory experiments, however mostly supervising Erik Elm Svensson. I was responsible for writing the paper. The paper was revised by all of the authors.

**Paper III** (Co-authors: Ersson A.G., Vosecký M., Järås S.G.)
In this paper I carried out some laboratory experiments, however mostly supervising Martin Vosecký. I was responsible for writing the paper. The paper was revised by all of the authors.

**Paper IV** (Co-authors: Thevenin P.O., Ersson A.G., Menon P.G., Järås S.G.)
This paper is a literature study and was written together by the authors. Philippe Thevenin was responsible and co-ordinator. The paper was revised by all of the authors.

**Paper V** (Co-authors: Ersson A.G., Thevenin P.O., Järås S.G.)
In this paper I carried out most of the laboratory experiments and was responsible for writing the paper together with Anders Ersson. The paper was revised by all of the authors.