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Circumventing fuel-NO_x formation in catalytic combustion of gasified biomass

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Abstract

It has been shown that it is possible to decrease fuel-NO_x produced from NH_3 using catalytic combustion of a synthetic gasified biomass at fuel-lean conditions. In a certain temperature regime where the conversion of fuel components, such as CO, H_2 and CH_4, is low and conversion of NH_3 is high, it is suggested that the formed NO_x is reduced by the remaining fuel components, mainly hydrocarbons. With oxide catalysts only ca. 10% of the NH_3 was converted to NO_x, the rest to N_2. It has also been shown that the ignition sequence of CO, H_2 and CH_4 varied for different catalysts and different experimental conditions, and that methane coupling and methanation reactions occurred before ignition of CH_4.

Keywords: Catalytic combustion; Gasified biomass; Fuel-NO_x; CO–H_2–CH_4 ignition

1. Introduction

Much interest in environmental aspects today focuses on electricity production from renewable energy sources, such as biomass, to reduce the net emissions of CO_2. At the same time, efforts are made world-wide to introduce catalytic combustion to reduce unburned hydrocarbons and emissions of NO_x, which causes acids rain and smog. In view of this, catalytic combustion of gasified biomass is considered to be a very promising technique for zero-emission electricity production.

Combustion of gasified biomass has a major advantage compared to combustion of solid biomass. The product fuel gas, mainly CO, CO_2, CH_4, H_2 and N_2, can be fed to a combined cycle, with combustion of the gasified biomass in a gas turbine followed by a heat recovery steam generator connected to a steam cycle. With this integrated gasification combined cycle (IGCC) technique, it is possible to achieve a very high electric efficiency with a high power-to-heat ratio in power plants. Therefore, IGCC is introduced in coal- and heavy oil-fired power plants throughout the world [1]. The commercial breakthrough for biomass-fired plants is still a few years ahead, mainly because of struggles with the introduction of a new technology. However, the technology is sufficiently advanced to justify large scale demonstration plants, which are needed for further developments in fuel gas cleaning (e.g. alkali, fuel nitrogen, sulphur, tars and particulates) as well as improved gas turbine specifications [2].

The main reason for using biomass as a fuel is that it is a renewable fuel with no net production of CO_2.

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This means that CO_2 is considered to be bound in a relatively short life-cycle, approximately 1–40 years, during the growth and combustion of the biomass. This could be compared to fossil fuels, where the CO_2 life-cycle is millions of years. In addition, biomass is a domestic commodity in countries, such as Sweden, with large supplies of wood or energy crops.

One of the problems that has to be addressed before the biomass-fueled IGCC can be fully commercialised is to lower the amount of NO_x formed from NH_3 in the fuel gas. Upstream catalytic ammonia destruction is at the development stage to solve this problem, e.g. a packed bed reactor with Ni- or Al-catalysts [3]. However, the idea proposed in this work is to solve the NO_x formation from NH_3 in the combustion chamber, with the use of a catalytic combustion chamber. This has three advantages. To begin with, a catalytic combustor that gives ultra-low emissions of thermal- and fuel-NO_x and in addition of CO and unburned HC (hydrocarbons), can run without post-combustion abatement units. Secondly, the low heating value of the fuel gas, approximately 5–7 MJ/Nm^3, may give rise to problems with flame stability within ordinary combustors, whereas catalytic combustors would stabilise the combustion process [4]. Finally, the number of reactors in the IGCC-unit can be reduced and the IGCC gas cleaning can be simplified.

The world-wide activities in catalytic combustion today [5–12], concentrate on natural gas as a fuel, because one of the major advantages of catalytic combustion versus flame combustion is the reduction of thermal-NO_x formed from N_2 and O_2 in air [13] at high temperatures. This is because the catalytic combustor stabilises combustion of lean fuel-air mixtures, thereby lowering the combustion temperatures to 1300–1400°C, compared to peak combustion temperatures of 1500–2000°C for a natural gas-fueled flame combustor. However, fuel-NO_x can also be formed if the fuel contains nitrogen species that react with the oxygen in air.

Fuel-NO_x abatement in catalytic combustion has been the focus for several research groups working with diesel and other nitrogen-containing fuels in the late 1970s and early 1980s. For example, Clark et al. [14] studied catalytic combustion of a synthetic low-heating value gas simulating gasified coal with addition of NH_3 to simulate fuel-N. A comparison between three pressurised combustion chambers, i.e. a catalytic combustor, a diffusion flame and a stirred reactor, showed that the catalytic reactor converted 14% of the ammonia to NO_x (86% to N_2), compared to 22–33% and 50% to NO_x for the diffusion flame and the stirred reactor, respectively. The NiO/ZrO_2-honeycomb catalyst was segmented with an addition of platina to the first segment to ignite the gas. The lowest conversion of NH_3 to NO_x was achieved when the catalyst was staged fuel rich – fuel lean with reduction of NH_3 in the fuel-rich region. A comparison with a Pt/Al_2O_3-catalyst showed that the $Pt/NiO/ZrO_2$-catalyst was superior during staged fuel rich/lean combustion [15].

Also, the group working with Ruckenstein studied catalytic combustion of propane doped with 1–4% ammonia in O_2/Ar over alumina-supported Cr_2O_3/Co_3O_4-catalysts at $0.8<\Phi<1.2$ and $460°C<T<640°C$ [16–18] where Φ is the actual fuel-to-air ratio to the theoretical fuel-to-air ratio. At temperatures above 600°C the emissions of unwanted nitrogen species (NO_x, NH_3, HCN) was reduced to 5–20% of the inlet concentration of NH_3, which was valid both for fuel-lean and fuel-rich combustion.

At our laboratory, catalytic combustion of a mixture of $CO/CO_2/H_2/CH_4$ has been studied over a shell-type Pt catalyst supported on alumina pellets [19]. CO and H_2 ignited simultaneously, with CH_4 having a higher ignition temperature, although CH_4-ignition was favoured by the presence of CO and H_2. It has been suggested that CO inhibits the ignition of H_2 by strong adsorption on the catalytically active sites. The combination of the fact that the Pt-catalyst converted practically all NH_3 to NO/NO_2 and the low thermal resistance of this catalyst showed that supported Pt catalysts are quite unsuitable for catalytic combustion of gasified biomass. Hence it is necessary to develop sintering-resistant non-noble metal combustion catalysts.

In the present work catalytic combustion of a synthetic gasified biomass has been studied, with emphasis on NH_3 conversion and ignition characteristics of the main combustible components CH_4, CO and H_2 over alumina-supported transition metal. To compare with previous work, transition metal oxides and noble metals have been studied as well. In addition, a synthetic diesel fuel has been tested, since it could come into consideration as a start-up fuel.

2. Experimental

2.1. Specifications of gasified biomass

The composition of biomass varies with the method of gasification and the composition of the raw biomass material. The composition of gasified biomass given in Table 1 is therefore an attempt to summarise the distribution of the main components. In addition to N_2, H_2, CO, CH_4, H_2O, C_2–C_{12} hydrocarbons and NH_3 as mentioned in Table 1, traces of HCN, sulphur and alkali components are detected in the gas. These trace components, along with H_2O and C_2–C_{12} hydrocarbons, were excluded for simplicity reasons. The remaining synthetic mixture was mixed with 200% excess air (λ=3), giving the composition of Table 1.

2.2. Gas analysis and activity testing

The activity testing and preparation of the different catalysts could be divided in four groups as summarised in Table 2 First, single metal oxides supported on alumina were tested with respect to conversion of $CO/H_2/CH_4$ and NH_3 in the synthetic gasified biomass described in Table 1. The gases were analysed with a Balzers QMG421-C Quadropole Mass Spectrometer and an Eco Physics CLD 700 EL-ht Chemiluminescence NO/NO_x analyser. These materials were tested in a tubular reactor in a furnace, with a 400 cells/in^2 cordierite monolith, 20 mm in length and 20 mm in diameter.

Second, a BaMn-hexaaluminate, a Pt/Al_2O_3 and a LaNi-perovskite supported on La-hexaaluminate were tested with respect to conversion of $CO/H_2/CH_4$ and NH_3 in the synthetic gasified biomass and analysed with a Shimadzu GC-3BT (for H_2) and a BOMEM MB100 Fourier Transform-InfraRed instrument with a DTGS-detector and a 4-meter beam-length White-cell for Infrared Analysis (for CO, CO_2, CH_4, C_2H_4, NH_3, NO and NO_2). The resolution was 1 cm^{-1}. Third, some transition metal substituted La-hexaaluminates were tested with respect to conversion of $CO/H_2/CH_4$ in the synthetic gasified biomass and analysed with the same quadropole mass spectrometer as for the first group of materials. The second and third groups of materials were tested in a tubular reactor with the catalyst washcoated on a mullite tube, Fig. 1.

Finally, the third group of material was tested with respect to conversion of a synthetic diesel fuel (80 wt% tetradecane as paraffin and 20 wt% α-methylnaphtalene as aromatic) and analysed by a ZRH infrared gas analyser for CO_2. Diesel fuels were tested in a tubular reactor in a furnace with a washcoated 400 cells/in^2 cordierite monolith, 35 mm in length and 21 mm in diameter.

2.3. Catalyst characterisation

The X-ray diffraction patterns, XRD, were recorded with a Philips diffractometer using monochromatised Cu K_α radiation, λ=0.15405 nm, scanning 2θ from 15° to 80°. The nitrogen adsorption measurements were made according to the Brunauer–Emmet–Teller method, BET, with nitrogen adsorption at liquid nitrogen temperature on a Micromeritics ASAP 2000.

Table 1
Composition of gasified biomass, laboratory synthetic gasified biomass and synthetic gas mixed with air

Component	Typical real gasified biomass (%)	Synthetic gasified biomass (%)	Synthetic gasified biomass mixed with 200% air (%)
N_2	41–50	42.0	73.4[a]
H_2	9–14	12.0	2.7
CO	14–18	16.0	3.6
CO_2	11–20	14.0	3.1
CH_4	5–7	5.0	1.1
H_2O	10–12	0.0	0.0
$C_{2–12}$	0–4	0.0	0.0
NH_3	200–3000	0–3000 ppm	0–600 ppm
O_2	0.0	0.0	16.0

[a] N_2 was replaced by Ar during QMS analysis.

Table 2
Catalyst preparation and activity testing (all activity runs performed at atmospheric conditions)

Catalyst (active phase/washcoat/substrate)	Reactor	SV (h^{-1})	Gas analysis[a]	Fuel[b]	Loading[c]	Ignition	NH_3 to NO_x	T (°C)
NiO/Al_2O_3/cordierite[d]	Monolith	25′	QMS/Chls	BG	1 g washcoat	$H_2<CO<CH_4$	14%[i]	500
Co–Cr oxide/Al_2O_3/cordierite[d]	Monolith	25′	QMS/Chls	BG	1 g washcoat	$H_2<CO<CH_4$	72%[i]	500
Co_3O_4/Al_2O_3/cordierite[d]	Monolith	25′	QMS/Chls	BG	1 g washcoat	$H_2<CO<CH_4$	79%[i]	700
Blank/Al_2O_3/cordierite[d]	Monolith	25′	QMS/Chls	BG	1 g washcoat	$H_2<CO<CH_4$	25%[i]	500
$BaMnAl_{11}O_{19}$/mullite[e]	Tube	70′	FT-IR/GC	BG	20 mg coating	$H_2<CH_4<CO$	33%[j]	700–800
$LaNiO_3/La_2O_3\cdot 11\ Al_2O_3$/mullite[f]	Tube	60′	FT-IR/GC	BG	20 mg coating	$H_2<CH_4<CO$	11%[j]	700-750
Pt/Al_2O_3/mullite[g]	Tube	60′	FT-IR/GC	BG	20 mg coating	$H_2<CO<CH_4$	74%[j]	300–800
Blank/mullite tube	Tube	70′	FT-IR/GC	BG	0 mg coating	$H_2<CH_4<CO$	12%[j]	720–750
LaMn-hexaaluminate/mullite[h]	Tube	10′	QMS	BG	50 mg coating	$CO<H_2<CH_4$	ND	–
LaCu-hexaaluminate/mullite[h]	Tube	10′	QMS	BG	50 mg coating	$CO<H_2<CH_4$	ND	–
LaCo-hexaaluminate/mullite[h]	Tube	10′	QMS	BG	50 mg coating	$CO<H_2<CH_4$	ND	–
LaNi-hexaaluminate/mullite[h]	Tube	10′	QMS	BG	50 mg coating	$CO<H_2<CH_4$	ND	–
LaMn-hexaaluminate/cordierite[h]	Monolith	50′	IR	C_XH_Y	0.7 g washcoat	Aromatic<paraffin	ND	–
LaNi-hexaaluminate/cordierite[h]	Monolith	50′	IR	C_XH_Y	0.7 g washcoat	Aromatic<paraffin	ND	–
Cordierite[h]	Monolith	50′	IR	C_XH_Y	0.0 g washcoat	Aromatic<paraffin	ND	–

[a] QMS – Quadropole mass spectrometer, Chls – Chemiluminescence, FT – Fourier transform, IR – Infrared.

[b] BG – Gasified biomass, C_XH_Y – Diesel.

[c] For NiO, Co–Cr oxide and Co_3O_4 mole loading is 4% of washcoat.

[d] Prepared by incipient wetness impregnation on alumina washcoated cordierite monolith, supplied by Svenska Emissionsteknik AB.

[e] BaMn–hexaaluminate powder supplied from Groppi et al. [22].

[f] Wet impregnation of La- and Ni-nitrate onto a co-precipitated La-hexaaluminate.

[g] Incipient wetness impregnation of Pt-chloride on alumina powder from Condea (Disperal, BET=173 m^2/g).

[h] Co-precip. of La- and Al-nitrates, calcination to 500°C, incipient wetness impregnation of Cu-, Ni-, Co- or Mn-nitrate, calcination to 900°C.

[i] Inlet concentration of NH_3 94 ppm, at temperature T.

[j] Inlet concentration of NH_3 500–600 ppm, at temperature T.

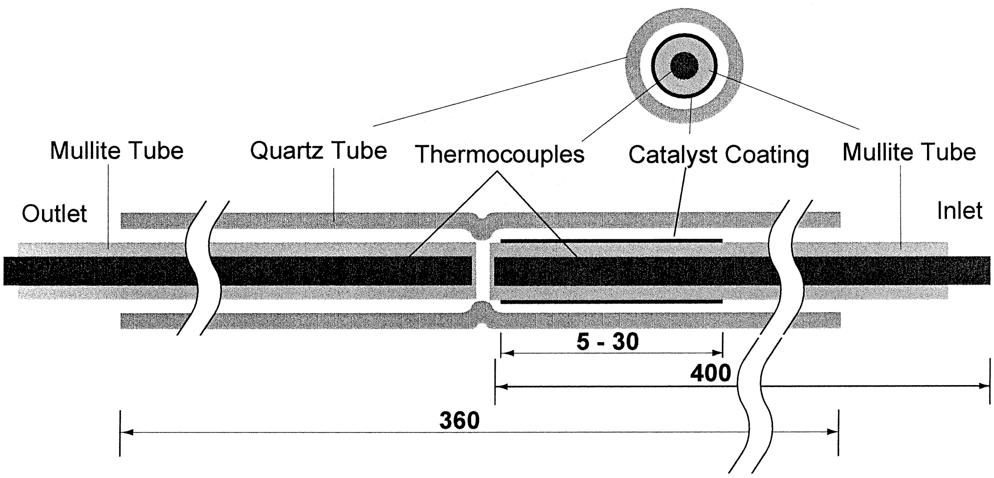

Fig. 1. Tubular reactor with a washcoated tube. Outlet could be a capillary tube instead of a thermocouple tube. Used under conditions as depicted in Tables 1 and 2.

3. Results and discussion

One of the main objectives was to study the ignition of CO, H_2 and CH_4. The results depicted in Table 2 show that CO, H_2 and CH_4 ignite in a different sequence and at different temperatures depending on catalyst type and space velocity at constant inlet composition. It is evident that the light-off starts at higher temperatures at higher space velocities, Figs. 2 and 3. The results reported here also show that CO controls the light-off of H_2 at low space velocities, Fig. 2, in agreement with earlier results on Pt/Al_2O_3 [19], followed by H_2 and CH_4. However, at higher space velocities H_2 controls the ignition, followed by CH_4 and CO, Fig. 3. The strong adsorption of CO at the active sites and consequent control of the ignition might not be seen at the higher temperatures needed for light-off at higher space velocities. At these tem-

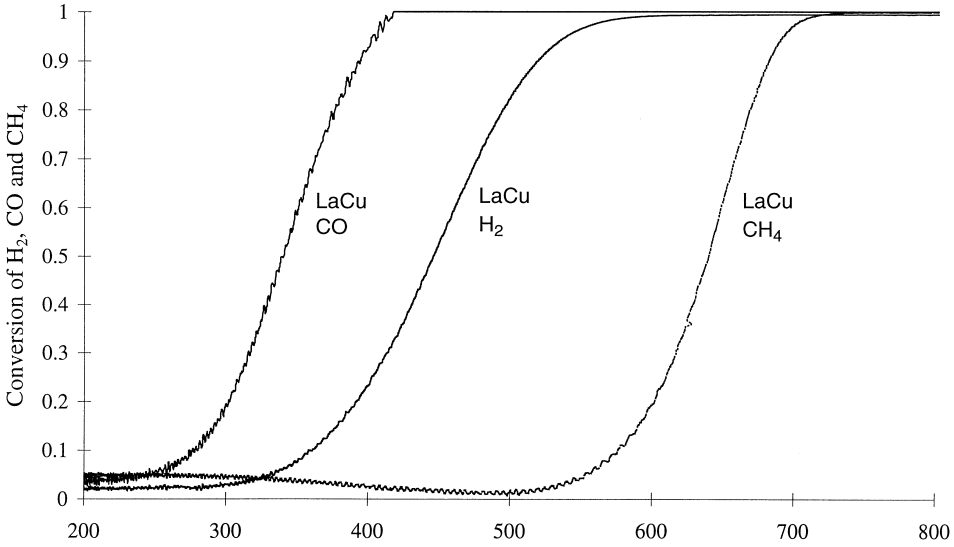

Fig. 2. Conversion of CO, H_2 and CH_4 over LaCu-hexaaluminate. Conditions as mentioned in Tables 1 and 2.

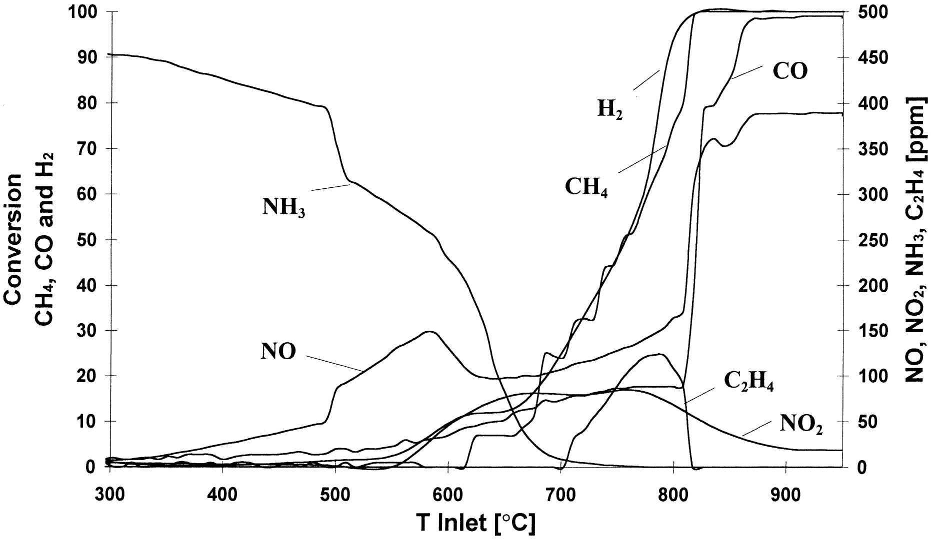

Fig. 3. Conversion of CO, H_2 and CH_4 and emissions of NO, NO_2, NH_3 and C_2H_4 over BaMn-hexaaluminate. Conditions as mentioned in Tables 1 and 2.

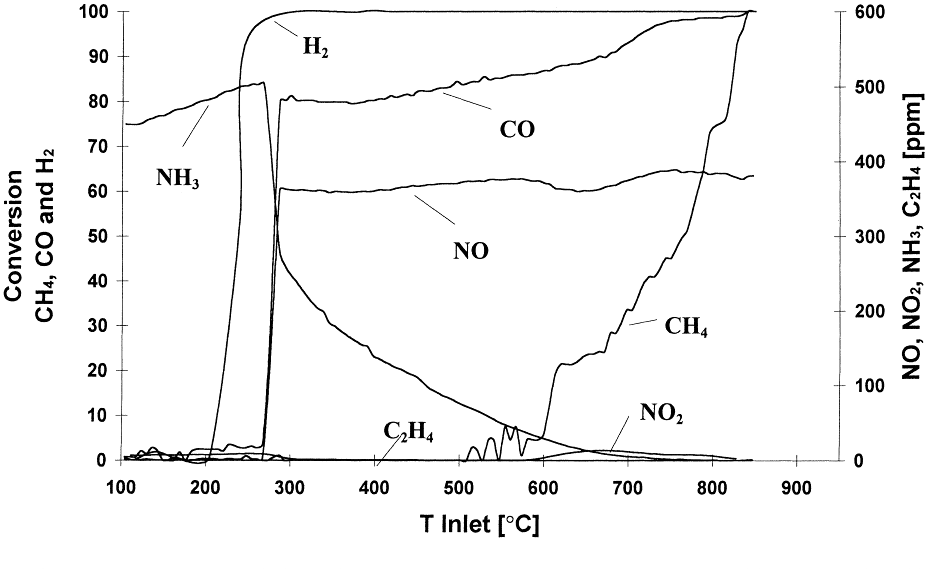

Fig. 4. Conversion of CO, H_2 and CH_4 and emissions of NO, NO_2, NH_3 and C_2H_4 over Pt/Al_2O_3. Conditions as mentioned in Tables 1 and 2.

peratures H_2 can compete with CO for the active sites, since the nature of the surface species changes at higher temperatures. This could explain why H_2 ignites first, followed by CH_4 rather than CO.

Further, it can be seen from Fig. 4 that Pt/Al_2O_3 is much more active than the hexaaluminate materials. Also, high surface-area alumina-supported single metal oxides are more active than complex hexaaluminate-type oxides, but are perhaps not stable enough at the high temperatures needed for catalytic combustion. NiO/Al_2O_3 together with Al_2O_3 were the most promising catalysts in the first group of materials, with respect to NO_x-abatement. NiO has been studied by others, as described in Section 1, and has been found to be promising at fuel-rich conditions [14] or in applications running on 100% fuel and no air before the combustion chamber [3,20]. The present work indicates that NiO catalysts also could be useful at fuel-lean conditions. The Cr_2O_3/Co_3O_4-catalyst and the Co_3O_4-catalyst showed high conversions of NH_3 to NO_x. However, earlier results showed that also the Cr_2O_3/Co_3O_4-catalyst could be interesting [16].

Methane coupling and methanation reactions are likely to occur in these experiments. It can be seen in Fig. 3 that C_2H_4 is produced between 700°C and 800°C, slightly before CH_4 and CO light-off. In Fig. 2 it can be seen that methane conversion goes down before light-off. This is not a true decrease in conversion, instead it equals a CH_4 production from CO and H_2. Approximately 0.05–0.10% CH_4 is produced. However, for simplicity reasons it has been plotted as a decrease in methane conversion. This indicates that there are a lot of active surface species before CH_4 light-off.

The lowest conversions of NH_3 to NO_x ($NO+NO_2$) are summarised Table 2. There is usually a temperature regime where the conversions of CO, H_2 and CH_4 are low and the conversion of NH_3 is high, but the yield of NO_x is still low, Figs. 2 and 3. Higher inlet temperatures and consequently higher conversions of CO, H_2 and CH_4, result in an increased yield of NO_x, typically 90% of the inlet concentration of NH_3. But, in a certain temperature interval, conversions of NH_3 are high, >90%, but only 10% is converted to NO_x and the remaining 90% being converted to N_2. Other nitrogen compounds, i.e. HCN or N_2O, were never detected at higher concentrations than about 5 ppm, i.e. close to the detection limit of the instrument. The mechanism for conversion of NH_3 to N_2 is not fully understood. At least one or more molecules are involved in the conversion of one NH_3 molecule to either NO_x or N_2. Since most of the NH_3, approximately 60–90%, is converted to NO_x at high temperatures and high conversions of CO, H_2 and CH_4, it is suggested that most of the NH_3 is also converted to NO_x at low temperature, and then in turn reacts with unburned fuel components, e.g. CH_4 and CO in a SCR-like reaction with N-free reductants [21]. However, in comparison to SCR-conditions in flue gases, the concentrations of fuel components that can be used as reductants are much higher, i.e. 1–5% unburned fuel compared to ca. 500 ppm NO_x.

Hence the first segment in the catalytic combustor could be a catalyst with a high selectivity for conversion of NH_3, but low conversions of fuel components, which would give low emissions of fuel-NO_x from NH_3. This implies that the first segment in the catalytic combustor should be a medium activity material

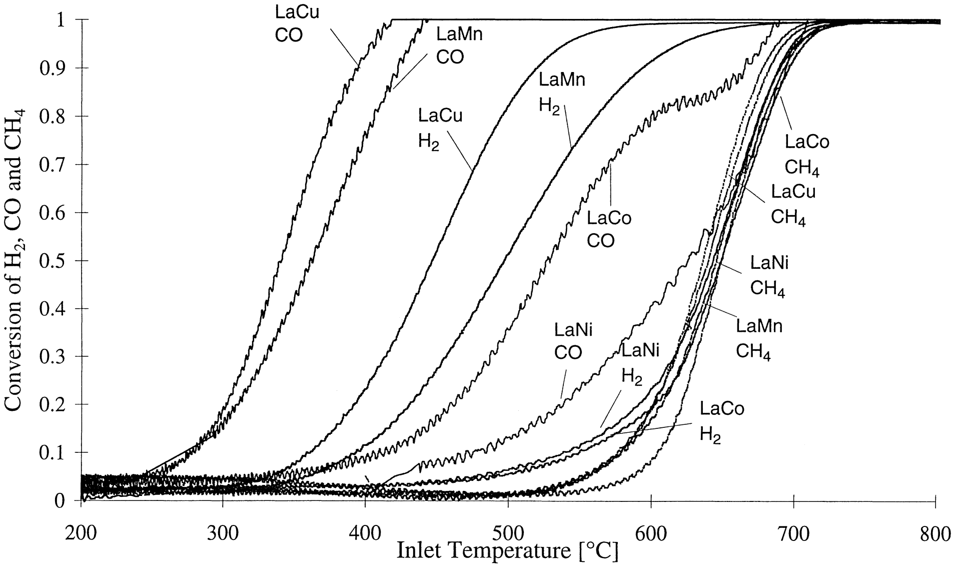

Fig. 5. Conversion of CO, H_2 and CH_4 over LaNi-, LaCu-, LaMn- and LaCo-hexaaluminate. Conditions as mentioned in Tables 1 and 2.

exhibiting rather low conversions of the fuel components. The work on transition metal-substituted La-hexaaluminates showed that a catalyst, such as LaCu-hexaaluminate, represented in Fig. 2, showed a very wide temperature difference between the ignition of CO and CH_4 as compared to Ni-, Mn- and Co-substituted La-hexaaluminates, represented in Fig. 5. Such a catalyst could give a low conversion of some of the fuel components, but high conversions of NH_3 and NO_x to N_2, and should be followed by a more active catalyst in the next segment.

Sulphur and alkali components in the gasified biomass could be considered as poisons to the catalyst, but these aspects have not been studied in this work. The additions of these poisons will be included in future catalyst testing.

Preliminary runs with a synthetic diesel fuel consisting of a mixture of aromatics and paraffins showed that aromatics ignited around 300°C followed by paraffins at 800°C. This indicates that it could be possible to see fuel-NO_x reduction by fuel-hydrocarbons when the fuel is only partly converted also with diesel fuels.

4. Concluding remarks

It has been shown that it is possible to decrease fuel-NO_x production in catalytic combustion of a synthetic gasified biomass in fuel-lean conditions, in agreement with earlier results on similar fuels. In a certain temperature regime where the conversion of fuel components, such as CO, H_2 and CH_4, is low and conversion of NH_3 is high, it is suggested that the formed NO_x is reduced by the remaining fuel components, mainly hydrocarbons. Typically, only 10% of the inlet concentration of NH_3 was converted to NO_x and the rest to N_2, over single and complex metal oxide catalysts. On the other hand, a Pt/Al_2O_3-catalyst converted 90% NH_3 to NO_x. It has also been shown that the ignition sequence of CO, H_2 and CH_4 varied for different catalysts and different experimental conditions, and that methane coupling and methanation reactions occurred before ignition of CH_4.

4.1. Future work

This work is going to continue in a three-year EC-funded project "Catalytic combustor for ultra-low emission dual fuel gas turbine - ULECAT", JOR3-CT96-0071, which is a co-operation between France, Italy and Sweden. ULECAT started 1 May 1996.

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