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Chemical Engineering Journal 91 (2003) 115–121

Chemical Engineering Journal

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Clean catalytic combustion of low heat value fuels from gasification processes

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Abstract

The conversion of biomass, coal and some waste materials by gasification offers an opportunity to utilise such fuel sources cleanly. Many of the aggressive species inherent in the fuel precursors can be retained in process, but one exception is nitrogen, which appears in the derived fuel gas generally as ammonia. Amounts of ammonia can be large, up to 3–4000 vppm from biomass [Combustion of Low Heating Value Gas in a Gas Turbine, Power Production from Biomass, Vol. II, Espoo, Finland, March 1995]. Heat values of the derived fuel gases depend on the process, but are typically one-tenth to one-half that of natural gas [Combustion of Low Heating Value Gas in a Gas Turbine, Power Production from Biomass, Vol. II, Espoo, Finland, March 1995; Catal. Today 27 (1996) 55; Fuel 71 (1995) 1363; Developments in Thermochemical Biomass Conversion, Blackie Academic and Professionals, London, 1997, pp. 817–827]. Although the derived gases can be water washed to give low contaminant levels (especially ammonia), typically 50 vppm; this creates a waste stream for disposal and represents a thermodynamic loss to the cycle.

Efficient conversion of gaseous fuels to electrical power is accomplished in gas turbines, preferably in combined cycle mode, where thermal efficiencies can be greater than 65%. Simple open cycle, high pressure ratio machines can achieve efficiencies greater than 40% and form the basis for Integrated Gasification Combined Cycles.

Primary issues for the gas turbine combustor when using gasification gases are:

- Their large volumetric flows;
- The fuel-bound nitrogen content represented by the ammonia fraction.

Fuel-bound nitrogen conversion in flame combustors can be large, even with stoichiometry control of the combustion process, where reduction to molecular nitrogen can be achieved to limit nitrogen oxides emission. The lowest levels of conversion to NO_x reported in turbulent flames are of order 20% of the input fuel-bound nitrogen content, and this will, in many cases, exceed the permitted range for nitrogen oxides emissions [Combustion of Low Heating Value Gas in a Gas Turbine, Power Production from Biomass, Vol. II, Espoo, Finland, March 1995; Ammonia formation and NO_x conversions with various biomass and waste fuels at the Varnamo 18 MWth IGCC plant, in: Proceedings of the Fifth Conference on Progress in Thermochemical Biomass Conversion, Tyrol, Austria, September 2000, pp. 17–22].

The paper describes experiments aimed at using catalytic combustion with reaction-specific catalysts to reduce the ammonia conversion rates, and so enable high levels of ammonia to be accommodated in the fuel gas without the disadvantages of waste disposal and thermodynamic loss to the engine cycle.

Keywords: Catalytic combustion; Low calorific value fuels; Fuel bound nitrogen; Gasification; Ammonia cleanup

1. Introduction

Microreactor studies [1] of a series of catalysts in a screening program were carried out at atmospheric pressure and using synthetic gas mixtures with CO/H_2 ratios lower than in typical fuel gas. The most promising formulation, which is a 2% Rh/Al_2O_3, was chosen as the best candidate to take forward for testing in a small scale high pressure test rig under conditions approaching those of a gas turbine. The catalyst substrate is cordierite honeycomb with square cells. The dimensions are 30 mm in diameter and 50 mm long with 400 cells per square inch. The monolith carries a washcoat of 22% La/Al_2O_3. The monolith is impregnated with rhodium nitrate solution and calcined in air at 500 °C, resulting in a 2% loading of rhodium on the surface as the active phase.

2. Experimental

The tests were carried out at ∼200 to ∼400 kPa, using synthetic coal gas as the fuel and blended from individual

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PII: S1385-8947(02)00144-4

Table 1
The specified target concentration of each component[a]

	vol.%	% mass
Nitrogen	46.40	3.59
Carbon dioxide	8.101	4.70
Water	9.10	6.75
Carbon monoxide	19.50	22.52
Hydrogen	15.10	1.25
Methane	1.80	1.19
Total	100.00	100.0

[a] Average net CV (MJ/kg): 4.36, average molecular mass (kg/kmol): 24.244, ammonia: 1500 ppmv, typical fuel gas temperature after gas cleaning and alkali removal is 450 °C.

components. The fuel contained the specified target concentration of each component as depicted in Table 1. In some experiments the CO_2 and H_2O were omitted: the reasons are considered under Section 3.

The catalyst selection and its performance were based on the results of two reactions:

(1) Addition of limited amount of oxygen (defined as process air) so as to promote the gas phase oxidation of NH_3 to NO

$$2NH_3 + \tfrac{5}{2}O_2 \rightarrow 2NO + 3H_2O$$

(2) The surface reaction of NO with CO at the Rh/Al_2O_3 interface whereby the NO is reduced to N_2

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

The aim of the small scale high pressure experiment was to determine the effect of temperature, pressure and H_2/CO content on the catalyst performance as the severity of the conditions increases so as to approach those of a gas turbine.

The fuel was blended cold using an 11-stream mass flow controllers set up. The fuel was heated using a 36 kW heater. The rig arrangement and fuel preparation prior to delivery to the catalyst are shown in Fig. 1.

The ballast N_2 was metered by a Coriolis meter. By virtue of the chemical reactivity of the ammonia, it was fed cold, i.e. bypassing the heater, so was the process air in order to avoid autoignition in the heater. Additional trace heating to the pipework leading to the catalyst was required in order to avoid excessive heat loss. The required catalyst operating temperature range was 700–800 °C.

The CO, H_2, CH_4, CO_2, H_2O together with the ballast N_2 made up the bulk of the fuel and was heated by a single pass through the heater. The small amount of oxygen required for the NH_3 to NO reaction came from the air injection. The oxygen content of the latter served a further purpose, which was to raise the catalyst bed temperature to

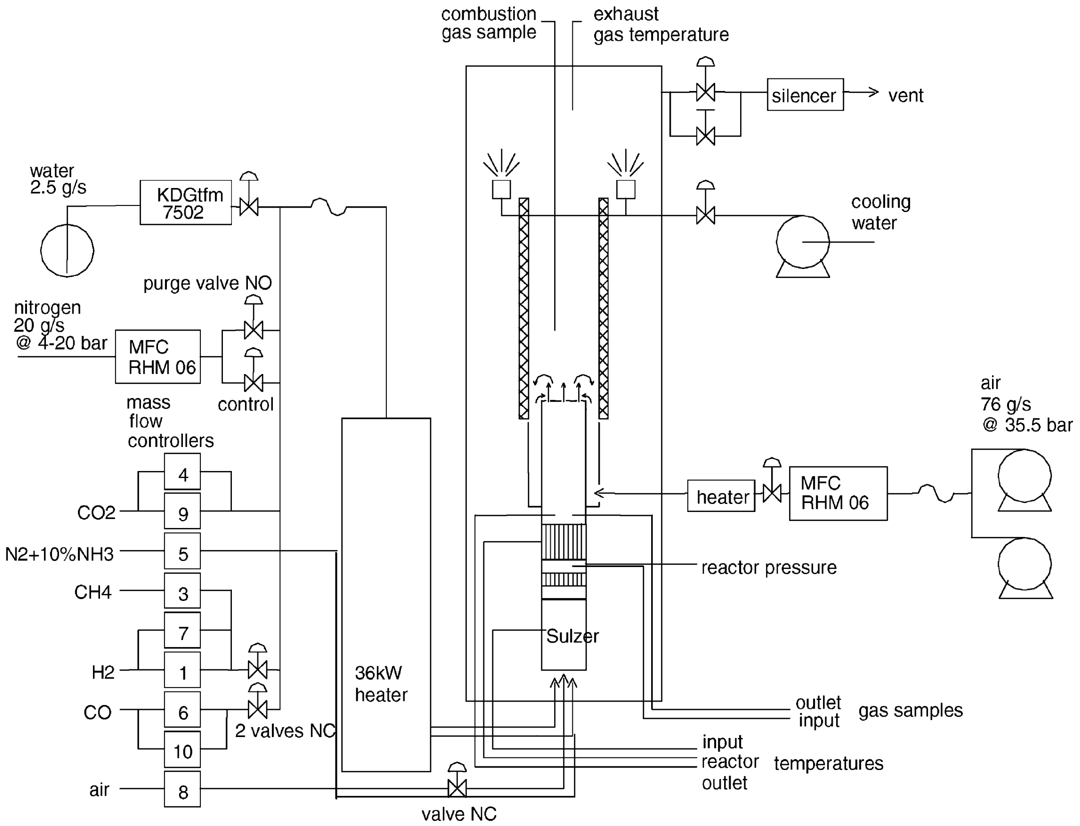


Fig. 1. High pressure small scale ammonia conversion experiment-system.

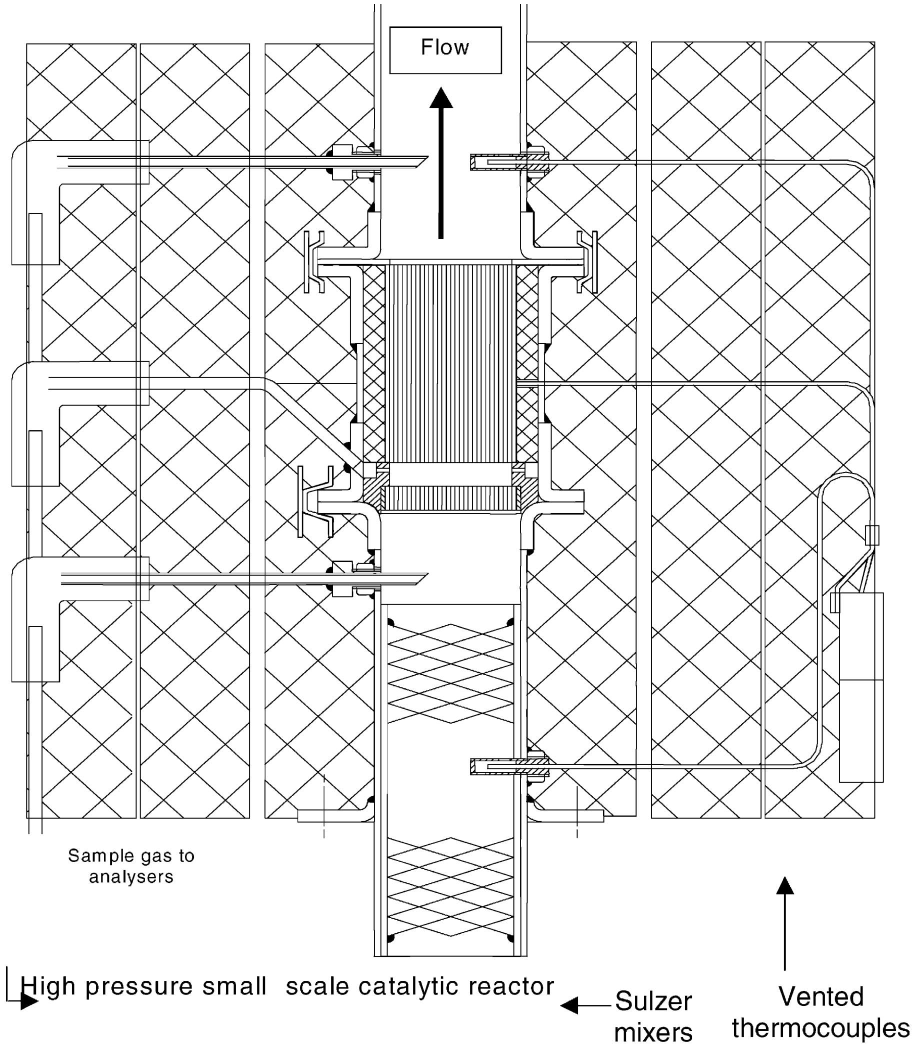


Fig. 2. High pressure small scale catalytic reactor.

the desired set point temperature, by combusting some H_2 on the catalyst surface. Each species competes at different rates for the limited amount of oxygen admitted, with nil left at the post-catalyst position.

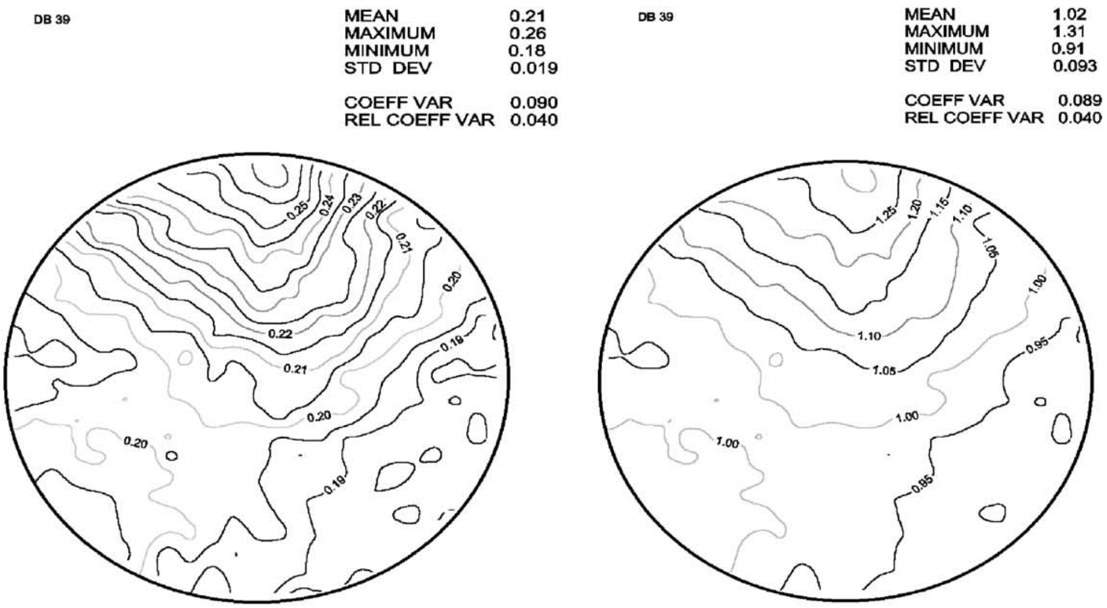
A spatially uniform mixture of all the fuel components with the process air in front of the catalyst is a prerequisite. Mixing was achieved by using two elements of a proprietary mixer (SULZER type SMV) in line, in front of the catalyst. A small section of the blank monolith is placed between the mixer and the catalyst. It acts as a flow straightener by removing the undesirable large flow structures that remain after mixing. Fig. 2 shows the mixer assembly together with the thermocouple positions, pressure transducer locations and the sample gas offtake positions.

The mixing quality has been quantified under a separate study [2]. Measurements of conserved scalar, helium, were made in a super-scale isothermal model at representative Reynolds numbers and flow rates equivalent to the likely rich and weak operating regimes of a typical gas turbine combustor. The recommended mixer assembly adopted in this study is one where the fuel is distributed perpendicular to the direction of alignment of the upstream element of the mixer and gave satisfactory mixing quality. Figs. 3 and 4 show mixedness profiles for the mixed flow before the monolith reactor. The point scalar concentration measurements have been multiplied by the corresponding local streamtube velocities to give a “flux parameter”. The flux parameter represents the arrival rate of reactants to the monolith and will be used to model the effects of mal-distributed flow on the reactor performance. The scope of that work is outside the range of this paper. Flow quality is fairly uniform between the conditions of interest.

Due to the reactivity of the constituents that make up the fuel, some pertinent reactions have become apparent. These reactions are listed below:

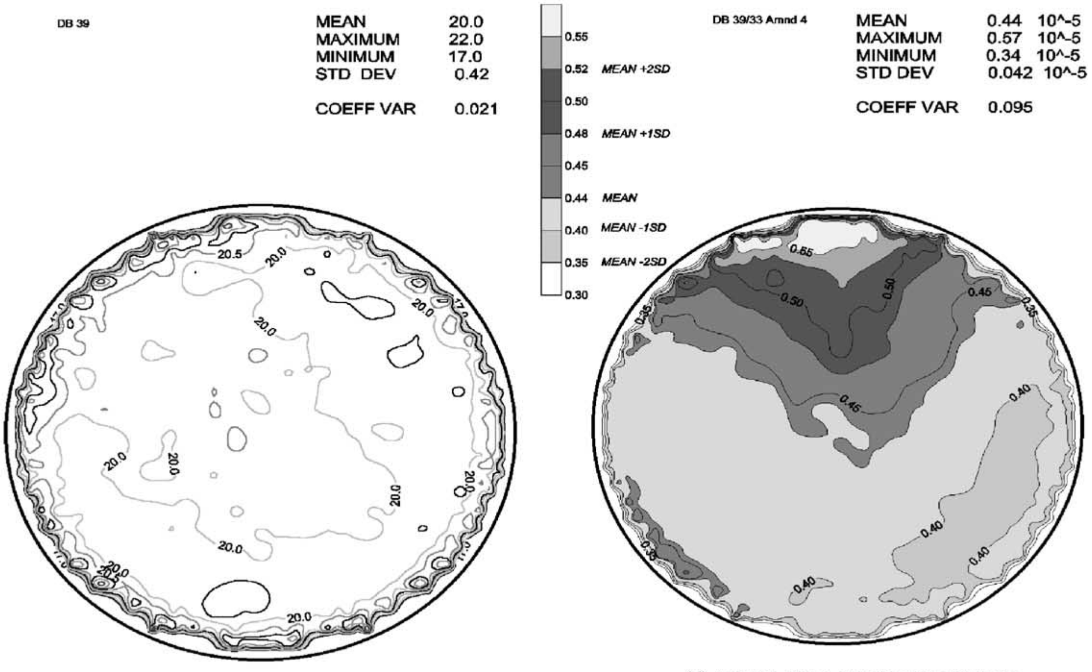
- Water gas shift in the heater

$$CO + H_2O \rightleftarrows CO_2 + H_2$$



(a) *LOCAL FUEL CONCENTRATION PARAMETER*
HeNl / HeNp

(b) *LOCAL MIXEDNESS PARAMETER*
HeNl / HeNt



(c) *LOCAL VELOCITY - m/s*

(d) *LOCAL FUEL FLUX PARAMETER*
(mHeN)l / HeNp - 10^-5 kg/s mm^2

Fig. 3. Views looking upstream, weak AFR simulation (Qs/Qp = 4.0), mean velocity 20 m/s, $V_{1\mathrm{mean}} = 6.0$ m/s, duct diameter 113.9 mm.

- Steam reforming in the heater

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

- Ammonium carbamate formation

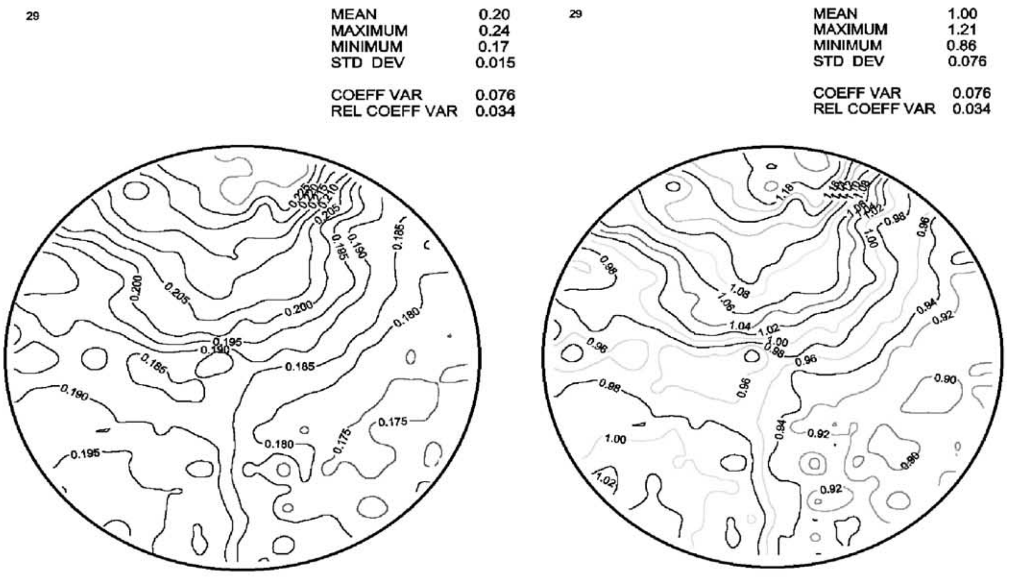
Ammonium carbamate ($NH_4NH_2CO_2NH_4HCO_3$) is formed at room temperature by reacting NH_3 with CO_2. It is a white crystalline powder that sublimes at 95 °C and is corrosive.

- Ammonia is highly soluble in water

$$NH_3 + H_2O \rightarrow NH_4OH\,(aq)$$

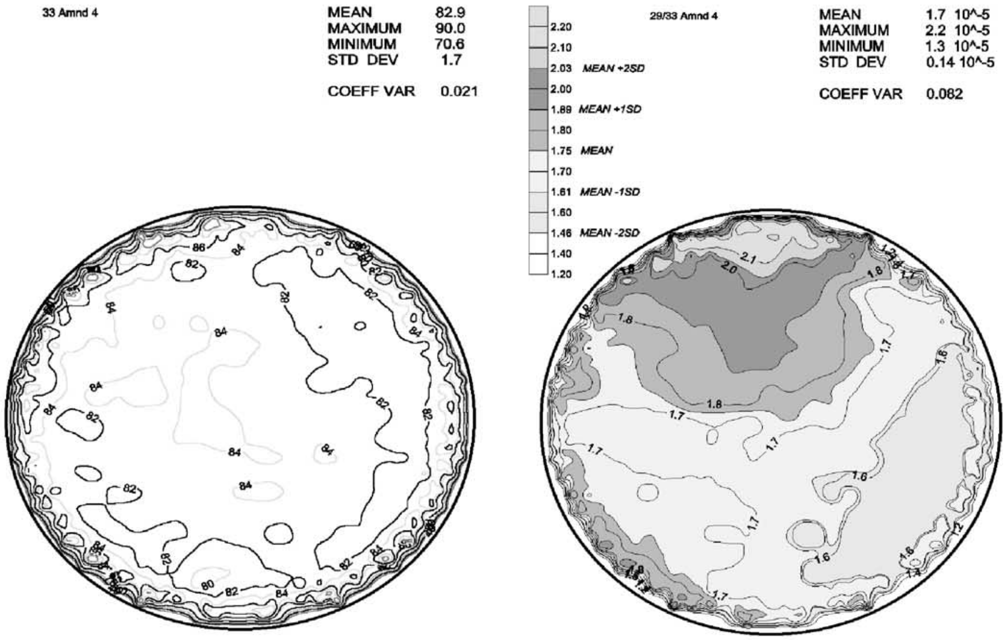
- Autoignition of the fuel/air mixture

In running the small scale high pressure testing facility, all the reactions identified above have been considered in order to provide a safe working methodology and to generate reproducible data on catalyst performance. The sample



(a) *LOCAL FUEL CONCENTRATION PARAMETER HeNl / HeNp*

(b) *LOCAL MIXEDNESS PARAMETER HeNl / HeNt*



(c) *LOCAL VELOCITY - m/s*

(d) *LOCAL FUEL FLUX PARAMETER (mHeN)l / HeNp - 10^-5 kg/s mm^2*

Fig. 4. Views looking upstream, weak AFR simulation (Qs/Qp = 4.0), mean velocity 38 m/s, $V_{1\mathrm{mean}} = 23$ m/s, duct diameter 113.9 mm.

gas was taken off at the catalyst upstream position (inlet composition) and at the catalyst downstream position. The sample lines leading to the analysers were kept hot with external electrical heating. The valves and the particulate filters were housed in a hot oven, thus ensuring the integrity of the samples. NH_3 was measured by an electrochemical method, using a solid state NH_4^+ ion electrode alongside FTIR measurement of the sample gas. Additionally, NO_x was measured by chemiluminescence, CO by infra red, CH_4 by FID, and H_2 by thermal conductivity. The high levels of nitrogen in the full fuel composition prevent accurate discrimination between measured inlet and outlet N_2 concentrations. The results are tabulated in Table 2.

3. Discussion

Ammonia conversion of the order 35–40% in the temperature range 600–700 °C was obtained at low CO/H_2 content in the fuel, in the sample gas at the post-catalyst section. The steady state NO_x levels measured at post-catalyst throughout the experiments were below 10 ppm. Below 600 °C

Table 2
The conversion of ammonia between inlet and measured outlet, expressed as percent conversion[a]

Notes	O_2 (g/s)	Fuel + air (g/s)	CO (vol.%)	H_2 (vol.%)	Inlet NH_3 (ppm)	Temperaturep bed, T (°C)	P (kPa)	NH_3 conversion (%)	Actual GHSV (h^{-1})
(a)	0.01	4.4	6.1	4.1	1423	514	160	Nil	185000
(b)	0.08	5.5	5.0	3.4	1363	616	160	37	231500
(a)	0.13	5.5	4.9	3.5	1042	740	175	40	231600
(c)	0.21	5.2	19.7	15.2	1748	730	180	33	249500
(c)	0.17	6.0	17.8	13.9	835	711	205	29	282000
(d)	0.28	6.5	16.6	12.9	869	784	220	27	295000
(c)	0.26	6.4	16.8	13.2	917	804	215	38	297500
(d)	0.28	14.7	17.9	13.9	1300	706	579	10	684000

[a] (a) Without H_2O and CO_2, low CO, H_2 concentration; (b) without H_2O, CO_2 and CH_4, low CO, H_2 concentration; (c) without H_2O and CO_2, with target concentration of remaining fuel components; (d) with full fuel blend with target concentration of all fuel components.

ammonia conversion was nil. The conversion increased with temperature, 38% conversion was achieved with the high CO/H_2 (as specified in the full fuel composition, Table 1, at 804 °C and 215 kPa. An activity drop of 10% was observed for a similar gas composition (target composition) but at reaction temperature of ~700 °C and pressure of ~200 kPa. The conversions observed under these conditions are manifestations of both SCR and SNCR reactions between NO and NH_3. At a higher operating pressure of 579 kPa and at 700 °C, the conversion achieved is only 10%, partly due to a high operating GHSV. The CO_2 and H_2O appear to act primarily as diluents. Reactor bed temperature and O_2 concentration are more significant, data blocks (c) and (d), Table 2.

The reaction schemes assume the following:

(i) That NO is prevalent in the presence of large excess H_2 by virtue of the selective gas phase oxidation of ammonia.
(ii) The rate of the surface reaction NO + CO is faster than (i) above for substantial conversion to be observed.

The above premise was tested by replacing the ammonia in the fuel with NO. The reaction was conducted in the pressure range 175–200 kPa. The results indicate that in presence of full fuel composition, the NO is converted to ammonia almost instantly in the 600–700 °C temperature window. It, therefore, follows that an SNCR reaction is probable at low H_2 where some ammonia is oxidised to NO, because of the low H_2; subsequently, the SNCR NO + NH_3 is favoured instead of NO + H_2 reaction.

The NO + CO catalytic reaction over Rh/Al_2O_3 works well in the automotive exhaust oxidation reaction, where the reaction takes place at atmospheric pressure and in the absence of large amounts of H_2. The interpretation of the experimental data obtained here suggests that the NO + CO catalytic reaction over Rh/Al_2O_3 is not applicable at high pressure and in the presence of a H_2 rich fuel, because the NH_3–N_2 reaction is dependent on three reactions.

$$2NH_3 + \tfrac{5}{2}O_2 \xrightarrow{Rh/Al_2O_3} 2NO + 3H_2O \tag{1}$$

$$2NO + CO \xrightarrow{\text{Low } H_2} N_2 + CO_2 \tag{2}$$

$$NO + \tfrac{5}{2}H_2 \xrightarrow{\text{High } H_2} NH_3 + H_2O \tag{3}$$

Reactions (1) and (3) favour NH_3 formation. When reaction (1) is conducted with NH_3 and air/N_2 only at ~200 kPa, and ~600 °C, copious amounts of NO were formed, but the reactions subsided almost instantly when H_2 was introduced and the product was mostly NH_3 as per reaction (3). To some extent reaction (2) is occurring at high temperature (700–800 °C) with low CO/H_2 gas composition and at ~200 kPa.

The selective catalytic conversion of NH_3–N_2 in presence of CO/H_2 has been reported in the literature [3–7], but with compositions which are remote from a gasified coal composition, and at atmospheric pressure, and the results are rather optimistic. The data presented here tend to confirm the finding that the selective catalytic oxidation of NH_3–N_2 is strongly inhibited by H_2/CO when adopting the NO route [3].

Acknowledgements

The authors are grateful for financial support provided under the UK Government's Foresight Challenge initiative, through the Office of Science and Technology, Grant Number GR/K 77235. The parent project title is "Clean Catalytic Combustion of Nitrogen-Bearing Low Heat Value Gaseous Fuels for Power and Heat Generation", with ALSTOM Power and Queens University Belfast as project partners. We also thank H.S. Rolfe, B. van Diepen and D. Binks for assistance with the experiments.

References

[1] Catalytic conversion of NH_3 to N_2, UK Patent G.B. 2 343 178.
[2] D. Binks, Design and determination of the mixing performance of an air mixer assembly, Internal Report, Combustor and Heat Transfer Technology Group, School of Engineering, Cranfield University, April 2001.
[3] M. Amblard, R. Burch, B.W.L. Southward, Clean catalytic conversion of nitrogen bearing gasified biomass, in: Proceedings of the Fourth International Workshop on Catalytic Combustion, San Diego, April 1999, pp. 14–16.

[4] L. Lietti, G. Groppi, C. Cristiani, P. Fotzatti, Ammonia oxidation during the catalytic combustion of gasified biomass fuel over Me-hexaluminate (Me = Mn, Co, Fe, Ni, Cr) catalysts, in: Proceedings of the Fourth International Workshop on Catalytic Combustion, San Diego, April 1999, pp. 14–16.
[5] L. Lietti, C. Groppi, C. Ramella, Catal. Lett. 53 (1998) 91.
[6] Development of Improved Stable catalysts and Trace Element Capture for Hot Gas Cleaning, Vol. 178, DTI/ETSU/Clean Coal Power Generation Group, Project Profile, 1996, p. 12.
[7] E.M. Johansson, S.G. Jaras, Catal. Today 47 (1999) 359.