Decomposition of Ammonia in IGCC Fuel Gas Streams

Shaik A. Qader (909) 466-6266
Qusro A. Qader (9o9) 466-6266
Energy and Environmental Technology Corporation
11609 Treviso Way
Rancho Cucamonga, California 91701

Lawrence J. Muzio (714) 859-4466
Fossil Energy Research Corporation
22342C South Pointe
Laguna Hills, California 92653

Introduction

Integrated Coal Gasification Combined Cycle (IGCC) technology has the potential to emerge as an efficient and environmentally clean technology for generation of power from coal. Development of processes to clean coal gas at high temperatures prior to its combustion in gas turbines improves efficiency and economics of IGCC technology. Particulate, NH_3, and H_2S comprise the main impurities of coal gas.

During combustion, NH_3 present in coal gas is oxidized to NO_X which necessitates NO_X removal from gas turbine exhaust using the expensive Selective Catalytic Reduction (SCR) process (Refs. 1-3). Decomposition of NH_3 present in coal gas at high temperatures prior to combustion results in higher IGCC efficiency and lower costs.

Ammonia can be removed from coal gas by scrubbing the gas with water or H_2SO_4 at a low temperature of 1500F (Ref. 4). Ammonia present in the flue gas of a large incinerator operating in Switzerland was reduced by injection of methanol at high temperatures in the range 1300-20000F (Ref. 5). Research on catalytic decomposition of NH_3 at high temperatures is also being carried out at Research Triangle Institute under DOE sponsorship (Ref. 6).

The Energy and Environmental Technology Corporation (EETC) is developing processes to decompose NH_3 at high temperatures, Bench-scale tubular flow reactors operating isothermally have been used to test two new approaches,

Objective

The main objective of the research work is to develop technically feasible and potentially low cost processes to decompose NH_3 present in coal gases at high temperatures upstream of the gas turbine. Specific objectives of the work include development of NH_3 decomposition processes applicable to both air-blown and oxygen-blown coal gasification-based combined cycle power plants,

Technical Approach

Ammonia decomposition tests were carried out in a bench-scale tubular flow reactor shown in Figure 1. The flow system includes feed gas supply with flow control and pressure regulation, preheater and reactor, heaters, monitoring and control of system temperature and pressure, and feed and product anal ysis instrumentation. Non-catal ytic NH_3 decomposition tests were carried out in both Alloy RA-330 and quartz reactors. Catalytic tests were conducted only in the quartz reactor.

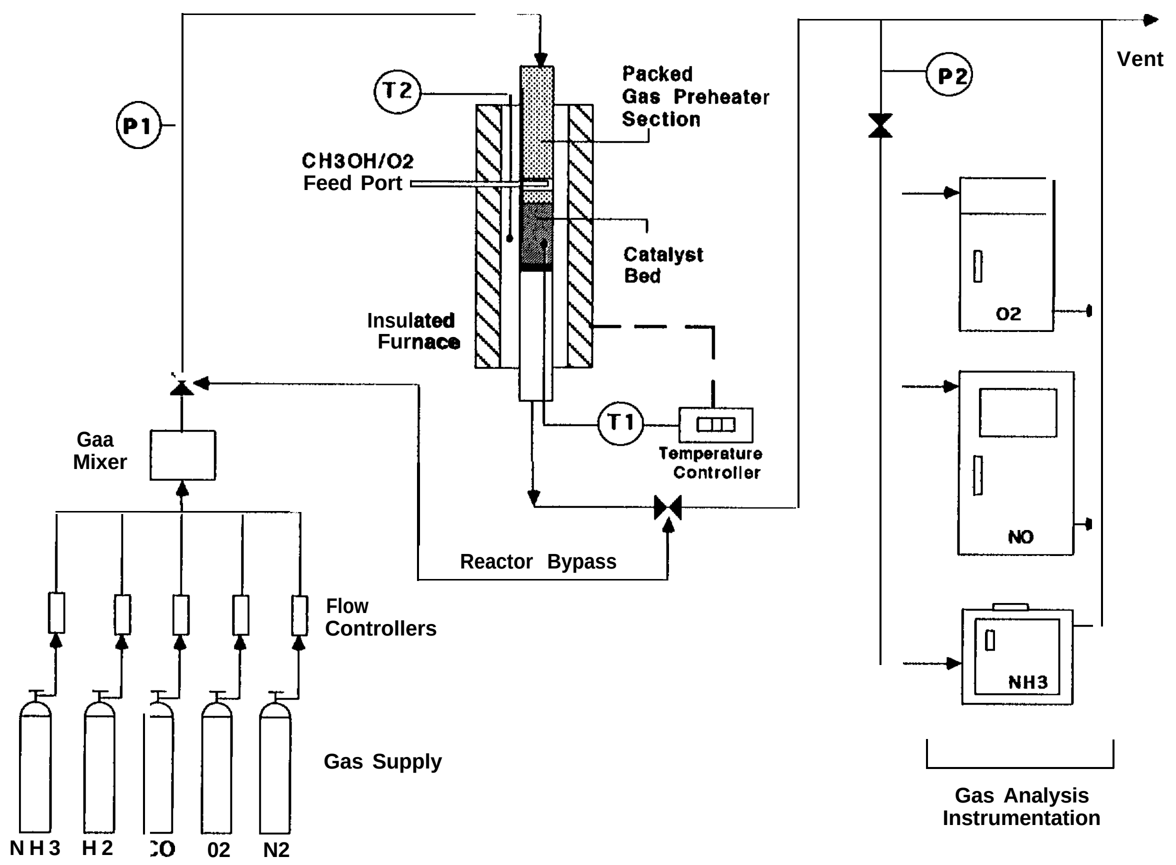

Figure 1. Schematic of Bench-Scale Flow System

Alloy RA-330 and quartz reactors of 0.25 in, -0.35 in. I.D. and 24 in. -36 in. length were used. The alloy and quartz reactors employed for non-catalytic NH_3 decomposition tests were packed with alloy and quartz packing, respectively, having an average diameter of 3 mm. For the catalytic tests, the quartz reactor was packed with alumino-silicate catalyst particles of 3-4 mm diameter.

Tests were carried out in three temperature ranges: 800- 10OOOF, 1200- 13000F, 1600”-18000F. The non-catalytic tests were performed in the two higher temperature ranges, and the catalytic tests were carried out in the lower temperature range. Ammonia decomposition tests were also carried out in the presence of H_2 and CO. Oxygen was used in the catalytic decomposition tests. Tests were designed to obtain data applicable to air-blown as well as oxygen-blown coal gasification-based IGCC systems. Gas analyses were done by standard methods.

Project Description

Two processes have been developed for decomposition of ammonia present in coal gases. In the first process, NH_3 undergoes decomposition on the surface of Alloy RA-330 in the temperature ranges of 1200- 13000F and 1500- 16000F. In the second process, NH_3 undergoes decomposition on the surface of an alumino-silicate catalyst in the temperature range of 800-10000F.

RA-330 Promoted Decomposition (RAPD) Process

Figure 2 shows the basic RAPD process concept. In this concept, coal gas containing NH_3 enters a reactor packed with RA-330 honeycombs in the temperature ranges of 1200- 13000F and 1500- 16000F. Ammonia is decomposed on the surface of RA-330 honeycomb. Some NH_3 may decompose in the gas phase. The technical feasibility of the concept was established by tests performed in the flow system using a RA-330 tubular reactor packed with RA-330 packing of 3-4 mm diameter pieces. The packing was used to provide surface for NH_3 decomposition, Tests were carried out in the presence and absence of methanol.

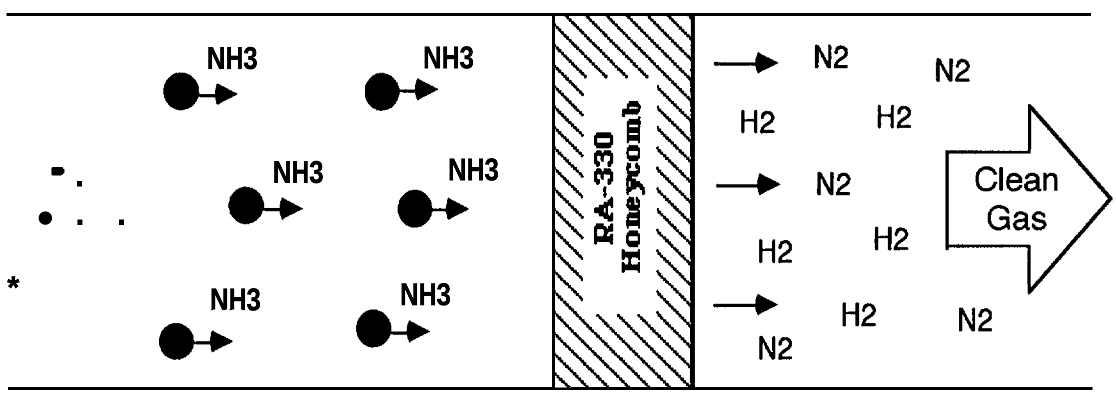

Figure 2. Basic RAPD Process Concept

Table 1 contains data which were obtained with methanol injection in the RA-330 reactor. The data show that total NH_3 conversion increases from **95%** at 10OOOF to greater than 99% at 13000F and above. However, 76% and 65% of the NH_3 was converted to amine as an intermediate product at 10000 and 12000F respectively. But at 13000F and above, all the NH_3 was ultimately decomposed to N_2 and H_2. If any amine was formed as an intermediate product, it may have decomposed at the higher temperatures. The data of Table 1 led to the conclusion that most of the NH_3 is converted to amine at temperatures in the range 1000- 12000F. At temperatures of 13000F and higher, NH_3 and any possible amine undergoes decomposition to nearly 10OO/O.

Table 1: Effect of Temperature on Ammonia Decomposition in RA-330 Reactor

CH_3OH/NH_3 moles = 1.0
Residence Time = 0.6- 0.8 sec.

Temperature (○)F	Total NH_3 Conversion (%)	NH_3 Conversion to Amine (%)
1000	**95**	**76**
1200	97	65
1300	>99	Trace
1600	>99	--
1800	>99	--

Table 2 contains data which were obtained with methanol injection in the quartz reactor. The total NH_3 conversions obtained at 1300 and 16000F are lower than the corresponding conversions obtained in the RA-330 reactor. Even at these high temperatures, most of the NH_3 is converted to amine which did not undergo decomposition.

Table 2: Effect of Temperature on Ammonia Decomposition in Quartz Reactor

CH_3OH/NH_3 moles = 1.0
Residence Time = 0.5- 0.6 sec.

Temperature (oF)	Total NH_3 Conversion (%)	NH_3 Conversion to Amine (%)
1300	80	70
1600	91	82
1800	>99	41

Table 3 contains data which were obtained in the RA-330 reactor without methanol injection. NH_3 decomposition of close to 100% was obtained at 13000F, 16000F and 18000F, which indicates that NH_3 decomposes directly to N_2 and H_2 on the surface of RA-330 which promotes the decomposition reaction.

Table 3: Effect of Temperature on NH_3 Decomposition

Reactor = RA-330 Alloy **Residence Time = 0.8 -1.0 sec.**

Temperature (oF)	NH_3 Decomposition (%)
1000	27
1200	44
1300	>99
1600	>99
1800	>99

The data of Tables 1-3 led to the conclusion that NH_3 decomposition by reaction with CH_3OH is not technically feasible due to the formation of amine as an intermediate product. The data also led to the conclusion that NH_3 can be completely decomposed on the surface of RA-330 without addition of CH_3OH.

Table 4 contains data which were obtained in the RA-330 alloy reactor at 1300 and 16000F in the presence of H_2 and CO. Hydrogen present in the gas reduces NH_3 decomposition. At 13000F, NH_3 decomposition decreases from greater than 99% at 0% H_2 to 85% at 19% H_2 and to 76% at 34% H_2. At 1600oF, NH_3 decomposition decreases from >99% at O% H_2 to 92% at 20!% H_2 and to 84% at 3 5°/0 H_2. Carbon monoxide does not seem to have any significant effect on NH_3 decomposition.

Table 4: Effect of H_2 and CO on Ammonia Decomposition

Reactor = RA-330 Alloy
Residence Time = 0.8 -0.9 sec.

Temperature (oF)	H_2 Concentration (%)	CO Concentration (%)	NH_3 Decomposition (%)
1300	19	0.0	85
1300	34	0.0	76
1600	20	0.0	92
1600	35	0.0	84
1300	20	30	86
1600	30	32	88

Application of RAPD Ammonia Decomposition Process

The test data of Tables 1-4 were evaluated to determine applicability of the RAPD concept for decomposition of NH_3 present in coal gas at high temperatures before the gas is fed to the gas turbine. The evaluation showed that the RAPD process is technically feasible and is applicable for decomposition of NH_3 present in coal gas at high temperatures upstream of the gas turbine. Figures 3 and 4 contain conceptualized schematics of the RAPD process.

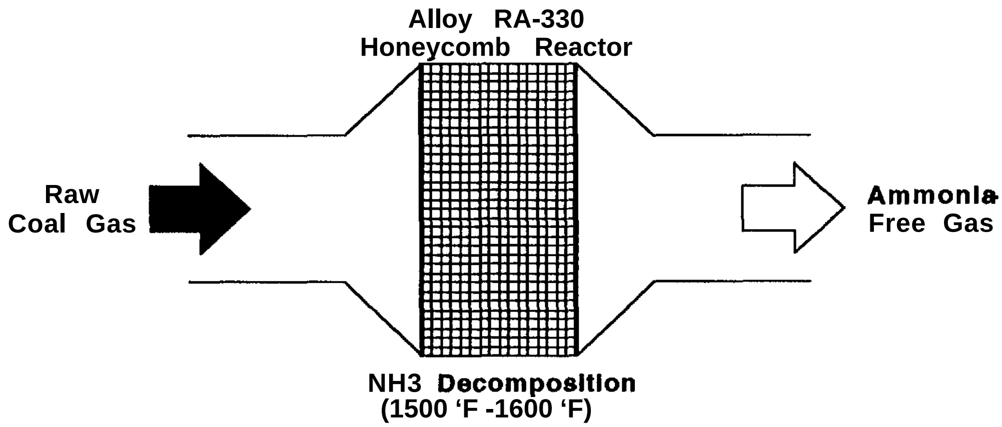

Figure 3. Schematic of High Temperature RAPD Process for NH3 Decomposition

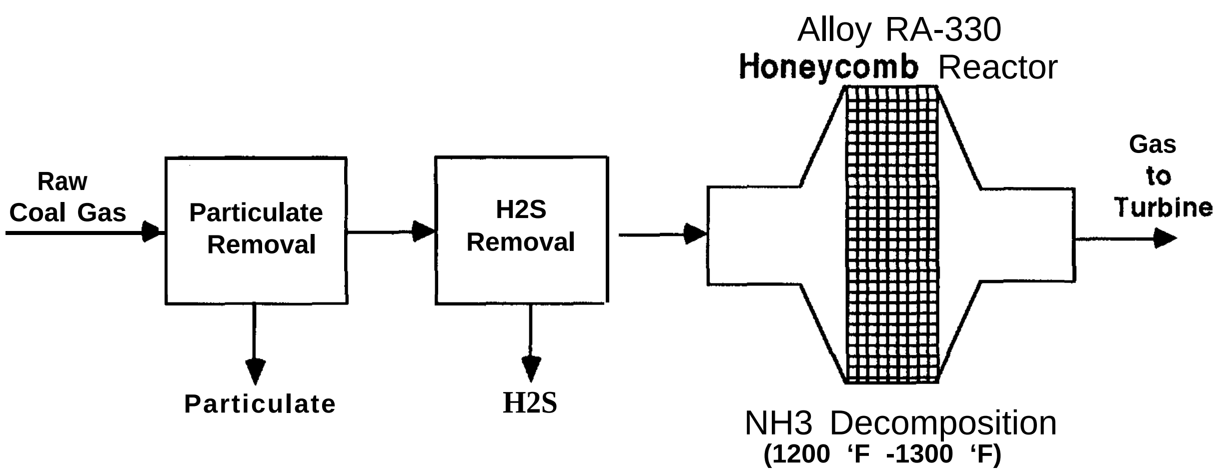

Figure 4. Schematic of Low Temperature RAPD Process for NH3 Decomposition

In the process scheme of Figure 3, coal gas enters the NH_3 decomposition reactor which contains a packed bed of RA-330 honeycombs at a temperature of 1500 - 16000F. Ammonia decomposes to N_2 and H_2 on RA-330 surface which promotes decomposition. In the process scheme of Figure 4, coal gas, after removal of particulate and H_2S, enters the NH_3 decomposition reactor which contains a packed bed of M-330 honeycombs at a temperature of 1200-13 00oF. Ammonia decomposes to N_2 and H_2 on RA-330 surface which promotes decomposition,

Table 5 contains NH_3 decomposition data applicable to IGCC technology. Ammonia decomposition depends upon temperature and H_2 concentration in the coal gas. At H_2 concentration of 19-20°/0, which is characteristic of air-blown coal gasification processes, NH_3 decomposition of 80-85% can be obtained at 1200- 13000F. At H_2 concentration of 30-35%, which is characteristic of oxygen-blown coal gasification processes, NH_3 decomposition of 85-90% can be obtained at 1500 - 16000F.

Table 5: RAPD Ammonia Decomposition Process - Application to IGCC Technology

Temperature (oF)	H_2 Concentration (%)	NH_3 Decomposition (%)	Potential Application
1200-1300	19-20	80-85	Air-blown gasification based IGCC technology
1500-1600	30-35	85-90	Oxygen-blown gasification based IGCC technology

These NH_3 decomposition percentages are calculated from raw experimental data. There is potential to improve NH_3 decomposition rates by providing more surface for decomposition and by optimizing process conditions,

Catalytic Ammonia Removal (CAR) Process

Figure 5 contains a schematic of the CAR process for removal of NH_3 from coal gas. In this process, coal gas free of particulate and H_2S enters the reactor in the temperature range of 800-1000oF. Air or oxygen is injected into the gas stream before it enters the catalyst bed. The process uses commercially available honeycomb catalysts, The technical feasibility of the process was established by performing tests in the flow system (Figure 1) using a quartz tube packed with an alumino-silicate catalyst of 3-4 mm pieces cut from a honeycomb. Tests were carried out in the temperature range of 850- 10000F in the presence of H_2 and O_2.

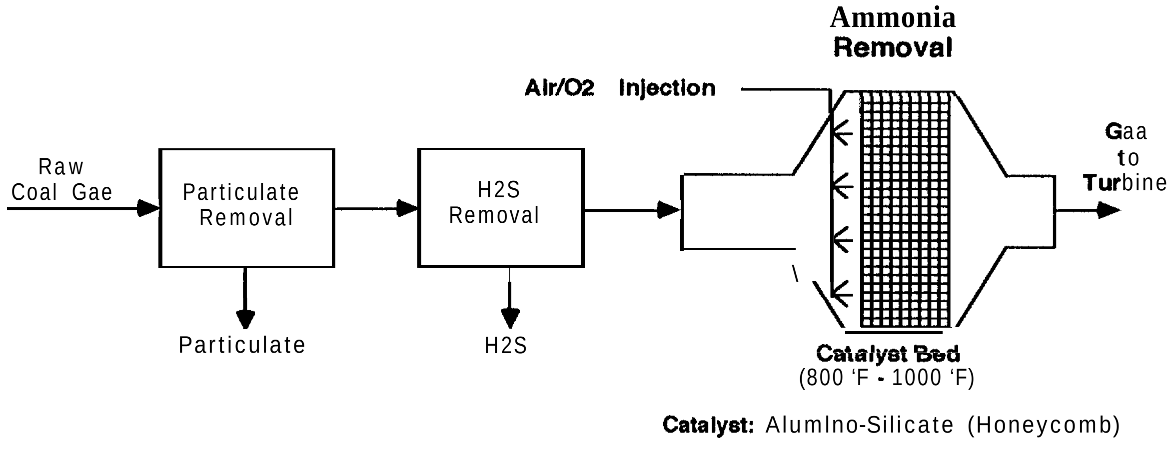

Figure 5. Schematic of Catalytic Process for NH3 Removal

Figure **6** contains process data obtained at 8500F and residence time of 0.5 -0.6 seconds. The data show that NH_3 conversion decreases with increase in hydrogen concentration but increases with increase in O_2 concentration. At H_2 concentration of 10-20°/0, 85-90°/0 of NH_3 can be removed by maintaining O_2 concentration of 2.0- 2.5%. At H_2 concentration of 30-35%, NH_3 conversion of only 50-70°/0 was obtained in the same O_2 concentration range. More O_2 is required to get higher ammonia conversion at higher H_2 concentration.

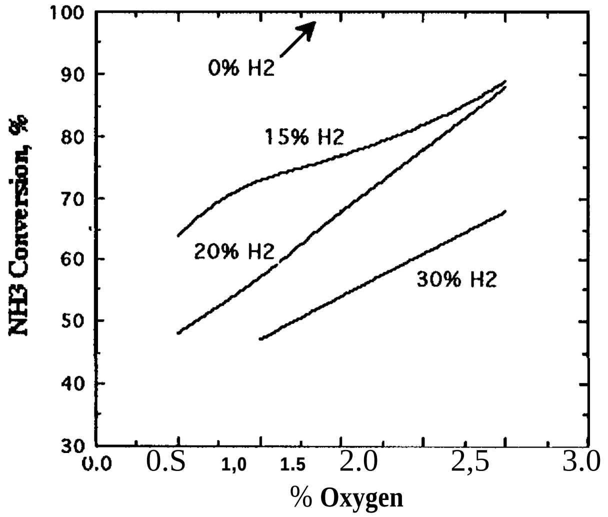

Figure 6. Effect of H2 and 02 on NH3 Removal at 850 F

Figure 7 contains process data obtained at 9000F and residence time of 0.5 -0.6 seconds, The data show similar effects of H_2 and 0_2 on NH_3 removal as the data of 8500F showed. Ammonia removal decreases with H_2 concentration but increases with O_2 concentration, However, higher NH_3 conversions were obtained at 9000F when compared to conversions obtained at 850oF. At H_2 concentration of 10-20°)6, 85-95°A of NH_3 can be removed by maintaining O_2 concentration of 2.0- 2.5%. At H_2 concentration of 30-35%, 65-70% of NH_3 can only be removed at O_2 concentration of 2.0- 2.50/o.

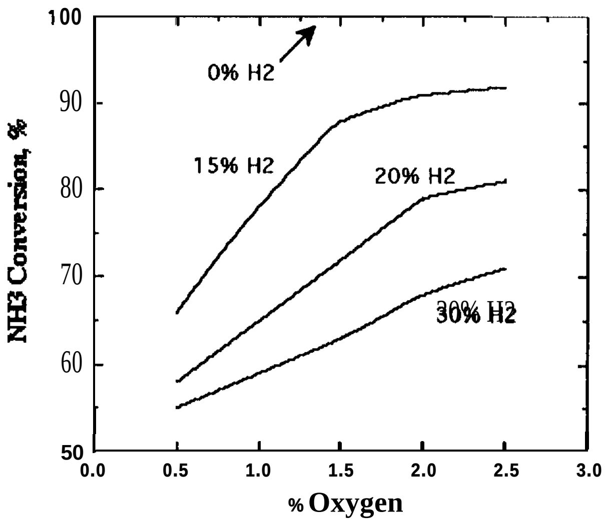

Figure 7. Effect of H2 and 02 on NH3 Removal at 900 F

Figure 8 contains process data obtained at 950 and 1000oF at H_2 concentration of 35%. At 9500F, NH_3 removal of 70-80% was obtained at 0_2 concentration of 2.0- 2.5%. Ammonia removal has increased at 10000F. At O_2 concentration of 2.0- 2.5%, NH_3 removal of 85-95% was obtained.

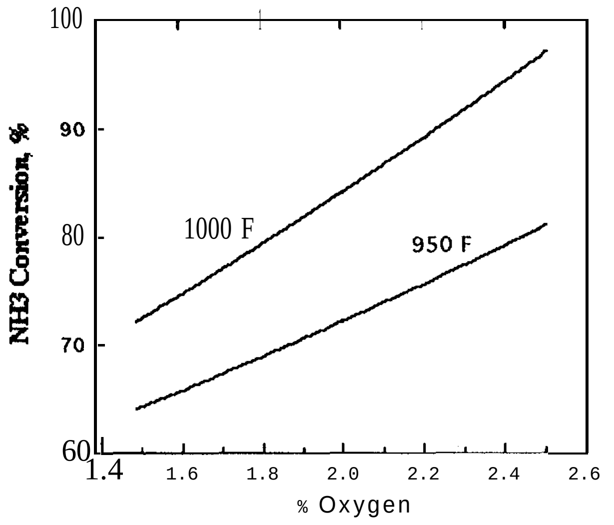

Figure 8. Effect of Temperature and 02 on NH3 Removal with 35% HZ

Application of Catalytic Ammonia Removal Process

The catalytic conversion data presented in Figures 6-8 and Table 6 show that the process has potential applications for NH_3 removal from both air-blown and oxygen-blown gasification based IGCC technologies. For air-blown gasification based application, 80-90% of NH_3 can be removed in the temperature range of 850- 9000F. For oxygen-blown gasification application, 85-95°/0 of NH_3 can be removed in the temperature range of 950- 10000F. In both cases, O_2 concentration of 2.0- 2.5% **is** required.

Table 6: Catalytic Ammonia Removal Process - Application to IGCC Technology

Hydrogen Concentration (%)	Temperature (oF)	Oxygen Concentration (%)	Ammonia Removal (%)	Potential Application
15-20	**850-900**	**2.0- 2.5**	**80-90**	Air-blown gasification based IGCC technology
30-35	**950-1000**	2.0- 2.5	85-95	Oxygen-blown gasification based IGCC technology

There is potential to further improve NH_3 conversion by increasing residence time and optimizing process conditions.

Accomplishments

The Energy and Environmental Technology Corporation developed two new process concepts for decomposition/removal of ammonia present in IGCC fuel gas streams. Bench-scale test data showed that the process concepts are technically feasible and are applicable to both air-blown and oxygen-blown coal gasification based IGCC technologies. The processes have potential for decomposing/removing ammonia by more than 90%.

Future Activities

More work needs to be done to determine the full potential of the NH_3 decomposition/removal processes. More bench-scale tests and scale-up of the processes are required to determine viability for practical applications. Cost estimates of the processes have to be made to determine cost saving potential when compared to removal of NO_X from gas turbine exhausts of IGCC plants.

Acknowledgement

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References

1. Schonbucher, B., *Reduction of Nitrogen Oxides from Coal-Fired Power Plants by Using the SCR Process. Experience in the Federal Republic of Germany with Pilot and Commercial Scale DeNO$_X$ Plants*, Proceedings of 1989 Symposium on Stationary Combustion Nitrogen Oxide Control, EPRI GS-6423, Vol. 2, 1989, p. 6A-1 to 6A-17.

2. Mori, T., and Shimizu, N., *Operating Experience of SCR Systems at EPDC's Coal-Fired Power Station*, Proceedings of 1989 Symposium on Stationary Combustion Nitrogen Oxide Control, EPRI GS-6423, Vol. 2, 1989, p. 6A-85 to 6A-104.

3. Roble, C. P., and Ireland, P. A., *Technical Feasibility and Cost of Selective Catalytic Reduction (SCR) NO$_X$ Control*, EPRI GS-7266, 1991.

4. Kohl, A., and Riesenfeld, F., *Gas Purification*, 4th Edition, Gulf Publishing Company, Houston, 1985.

5. Jones, D. G., et al., *Two Stage DeNO$_X$, Process Test Data from Switzerland's Largest Incineration Plant*, EPRI Report GS-6423, Vol. 2, 1989.

6. Stanby, R. K., *High Temperature Catalytic Ammonia Decomposition for Reducing Fuel Bound NO$_X$ in Integrated Gasification Combined Cycle Plants*, METC Internal Document, April 21, 1994.