

The Chemistry of the Thermal DeNO_x Process: A Review of the Technology's Possible Application to control of NO_x from Diesel Engines

By

Richard K. Lyon

rlyonheart@aol.com

Exxon Research and Engineering (Retired)

GE EER Corp (Semi Retired)

EER GC (Semi Retired)

Abstract This paper presents a review of the Thermal DeNO_x process with respect to its application to control of NO_x emissions from diesel engines. The chemistry of the process is discussed first in empirical and then theoretical terms. Based on this discussion the possibilities of applying the process to controlling NO_x emissions from diesel engines is considered. Two options are examined, modifying the requirements of the chemistry of the Thermal DeNO_x process to suit the conditions provided by diesel engines and modifying the engines to provide the conditions required by the process chemistry. While the former examination did not reveal any promising opportunities, the latter did. Turbocharged diesel engine systems in which the turbocharger is a net producer of power seem capable of providing the conditions necessary for NO_x reduction via the Thermal DeNO_x reaction.

Properties of the Thermal DeNO_x Reaction Early in the 1970s a conflict developed between the increasing public demand for stricter control of NO_x emissions from mobile and stationary sources and the availability of technologies to meet these demands. The author had the good fortune to work on this problem and to be in an organization which was willing to follow a promising discovery where it lead. At that time catalysts which allowed the selective reduction of NO by NH₃ in the presence of massive amounts of oxygen were known, but this approach involved obvious difficulties. The pressure drop through the catalyst bed could be excessive, the bed could become fouled or plugged or the catalyst could be deactivated by SO₂ or other impurities. Even if these difficulties could be managed, the catalyst bed would occupy a large volume. In some applications providing that volume would be difficult and in all cases this approach would be costly.

If, however, one could find a homogeneous gas phase reaction which reduced NO all the difficulties of catalytic reduction would be avoided. Diesel engines, gas turbines, boilers, furnaces and many other combustion systems necessarily operate with substantial amounts of excess air, producing an exhaust which contains orders of magnitude more O₂ than NO. Thus the gas phase reduction reaction must be selective, reducing the NO while leaving the much larger amount of O₂ unchanged. Furthermore the NO must be reduced to N₂ since other possible reduction products

would not be environmentally acceptable.

Reasoning that NO might more easily be converted to N_2 with a reducing agent that contained nitrogen, the author did a series of experiments in a small laboratory reactor. At that time there was nothing new about the gas phase reaction of NO and NH_3 or of O_2 and NH_3 or NO and O_2 . The kinetics of these three reactions had been studied thoroughly over a wide range of conditions¹ but the reaction kinetics of mixtures containing NO, NH_3 and O_2 had not been studied. From the literature it was clear that for the experimental conditions shown in Figure 1 mixtures of NO and NH_3 , of O_2 and NH_3 and of NO and O_2 would all be inert. Figure 1 shows, however, the three component mixture reacts rapidly, the NH_3 selectively reducing the NO in the presence of a massive excess of O_2 .

Figure 2 shows that this new reaction has a temperature window, i.e. it occurs only in a narrow range of temperatures. If the temperature is too high, the NH_3 oxidizes to form NO. If the temperature is too low, little or no reaction occurs. As Figure 2 also shows, adding some H_2 to the NH_3 shifts this temperature window to lower values but does not make it any wider.

The properties of the Thermal DeNOx reaction define the situations/applications in which it can be used to control NOx emissions. It must be possible to rapidly and completely mix NH_3 with the gas being treated. When this is done the gas must be at an average temperature in the range of 1300°F to 2000°F and the more uniform the gas's temperature the better.

Thermal DeNOx Process Costs and Requirements in Application to Boilers and Furnaces With a modest 1.5 to 1 excess of NH_3 over NO the Thermal DeNOx reaction is capable of reducing NOx to levels which in an ideal case would be very low. For NH_3 at \$290/ton this corresponds to a cost of \$161/ton of NOx removed. In some applications hydrogen is not needed but in others it is. For some of the latter applications it is readily available and inexpensive. In others hydrogen must be generated by NH_3 decomposition. For a situation in which H_2 at 2/1 ratio to NH_3 is needed, the NH_3 thus used would cost \$214/ton of NOx removed.

While the Thermal DeNOx Process has been successfully applied to numerous boilers, furnaces and other combustion systems, the total cost of the process has been much higher than the reagent costs and NOx reduction has typically been limited to 70%. This reflects the difficulties of providing the conditions the process requires in boiler/furnace retrofit rather than any inherent limitation of the chemistry. Mixing small amounts of NH_3 with the vast amount of flue gas passing through a boiler or furnace requires using a carrier gas, steam or compressed air, in substantial amounts and at substantial cost. The limitation to 70% reduction of NOx reflects the difficulty of applying the process in retrofit to boilers and furnaces. The temperature across any cross section of a boiler or furnace is nonuniform, partly in and partly out of the process's temperature window. This makes some

¹R. K. Lyon, Int. J. Chem. Kin. 8, 315-318 (1976) and references cited therein.

degradation of process performance inevitable.

Kinetics and Mechanism of the Thermal DeNOx Reaction The discovery of the Thermal DeNOx reaction was followed by studies of its mechanism by the author and his coworkers and by other research groups. The former efforts culminated in the development of a kinetic data base and of a computer model². The data base consisted of 742 data points distributed over a range of temperatures, reaction times, and initial concentrations of NO, NH₃, O₂, H₂ and H₂O. The computer model used a set of 31 elementary reaction rates. Of these 31 reactions 27 had rate constants which were accurately known or could reasonably be estimated because they had little effect on the model's predictions. By using the remaining 4 reaction rate constants as adjustable parameters it was possible to fit the data base with its 7% experimental uncertainty.

Subsequent work by other research groups (see Schmidt and Bowman and references cited therein³) resulted in the development of improved computer models. The number of elementary reactions used was increased to 127. These additional reactions while they are unimportant under the range of conditions used in the Thermal DeNOx process, improve the model because they allow it to make predictions beyond this range. The adjustable parameters used in our model were replaced with experimentally determined rate constants.

In this accepted mechanism NO is reduced by the NH₂ radical in a two channel reaction, i.e.



Melius and Binkley⁴ have done 2 BAC—MP4 calculations for the reaction of NH₂ with NO with the results shown in Figure 3. Initially an H₂NNO molecule is formed. When formed this molecule contains a large amount of vibrational energy. This energy allows the molecule to undergo a unimolecular rearrangement in which the first hydrogen from the NH₂ migrates to the oxygen. This converts the H₂NNO molecule to an HNNOH molecule, initially the trans isomer. This trans isomer can either decompose to form N₂H and OH or it can isomerize to the cis isomer. Once the cis isomer is formed the second hydrogen from the NH₂ can also migrate to the oxygen, and the molecule decomposes to N₂ and H₂O.

The ratio in which these two processes occur depends on the temperature, the HN₂ + OH channel increasing at the expense of the N₂ + H₂O channel as the temperature is increased. In the

² R. K. Lyon, Preprints of the Fuel Division, ACS, 32, 433 (1987)

³CC. Schmidt and C. T. Bowman, Combustion and Flame, in press

⁴ C. F. Melius and J. S. Binkley, 20th Symposium

temperature range in which the Thermal DeNOx reaction occurs reaction 1 is faster than reaction 2. The HN_2 produced by reaction 2 decomposes according to reaction 3.



The H atom thus formed can react to regenerate NH_2 radicals via reaction 4.



The sequence of reactions 2,3, and 4 has a chain branching factor of 2, but, the overall chain branching factor for 1, 2, 3, and 4 is $2(1 - \alpha)$ where α is the ratio of the rate constant for reaction 2 to the sum of the rate constants of reactions 1 and 2. Since reaction 1 is faster than 2, α is less than one. This means that for a self sustaining chain reaction to occur another reaction which provides additional chain branching is necessary. It is generally agreed that in the Thermal DeNOx process reaction 5 has that role



The chain cycle is then completed by reactions 6 and 7.



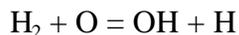
One piece of evidence showing that reaction 5 plays this critical role in Thermal DeNOx chemistry is the fact that Thermal DeNOx reduces NO in the presence of O_2 but not in its absence. The importance of reaction 4 is shown by the fact that as the concentration of NH_3 is increased the rate of NO reduction initially increases, but a point is reached at which the NO reduction stops.

The fact that the Thermal DeNOx chemistry has a lower temperature limit when NH_3 alone is used as the reducing agent is explained by the temperature dependence of reactions 1 and 2. As the temperature is decreased, the ratio of the rates of these reactions shifts in favor of reaction 1. More of the interactions of NH_2 and NO lead to chain termination rather than chain branching and maintaining a self sustaining chain reaction becomes more difficult.

Using NH_3 in mixture with H_2 eases this problem because the oxidation of H_2 is a chain branching process which can provide chain carriers to the reduction of NO by NH_3 . The chain cycle by which this happens consists of reaction 4 followed by reactions 8 and 9.



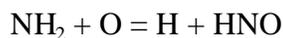
9



Reaction 5, however, has an activation energy of 16.5 kcal/mole. This limits the overall rate of the hydrogen oxidation chain reaction and hence as the temperature is decreased hydrogen oxidation becomes too slow to provide adequate chain branching and again there is a lower limit on the temperature of NO reduction.

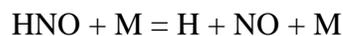
The fact that the Thermal DeNO_x chemistry has an upper temperature limit is explained by the competition between reaction 5 and reaction 10 below.

10



Since the HNO produced by reaction 10 quickly decomposes to NO and H via reaction 11,

11



the net result of reactions 10 and 11 is to convert NH₂ to NO. Thus by forming NH₂, NH₃ can react to reduce NO or can react to form it. For both NH₃ alone and for NH₃ + H₂ mixtures the rate of chain carrier production increases with increasing temperature. This increases the concentration of O atoms. Thus there is a point at which increasing temperature causes the balance between reducing NO via reactions 1 and 2 and producing it via reactions 10 and 11 to shift unfavorable.

The Possibility of Modifying Thermal DeNO_x Chemistry to suit Diesel Engines: The Use of NH₂R instead of NH₃ The exhaust from diesel engines is typically only 900°F, too cold for Thermal DeNO_x. One possible approach to overcoming this limitation is to look for another selective reducing agent, something which reduces NO in the same manner as NH₃ but which does so at a lower temperature. The discussion above may be summarized as follows: in Thermal DeNO_x NO is reduced by reaction with NH₂. The problem with using the NH₂ + NO reaction to control NO_x in diesel exhaust is that in this temperature range, even with the addition of hydrogen, it does not produce enough chain carriers for a self sustaining branching chain reaction. The history of chemistry shows many examples in which a chemical substance was found to have most but not all of the properties necessary for an important use and this recognition lead to the discovery of a related chemical substance with all of the necessary properties. Thus one possible solution to the problem of controlling diesel NO_x is to find a derivative of ammonia which has similar but more favorable properties.

If instead of using NH₃ an ammonia derivative, NH₂R, abstracting one of the hydrogens from the nitrogen will produce an NHR radical. NH₂ contains two hydrogens and either or both can migrate to the oxygen. That allows the reaction to occur by two channels, one channel which involves migration of one hydrogen atom producing nitrogen and two free radical chain carriers and the channel which involves migration of both hydrogen atoms producing the stable molecules nitrogen and water. One would expect the initial stages of the reaction of an NHR radical with NO to be analogous to the NH₂ with NO. Thus one expects the NHR + NO reaction to give rise to an HRNNO molecules which isomerizes to a trans RNNOH molecule. The trans RNNOH could isomerize to the cis form, but, unlike hydrogen, one would not expect the R group to be able to migrate. Thus the second channel is blocked

and the reaction of NHR with NO must all occur via the first channel, i.e. the NHR + NO reaction seems likely to yield N₂, OH and R. That means that each reaction of NHR and NO reaction might produces two free radicals chain carriers. A self sustaining chain reaction might then occur without the reaction 5. Consequently using NH₂R instead of NH₃ could allow a rapid chain reactions that reduces NO to molecular nitrogen at the temperatures available in diesel exhaust

Wenli, Dam-Johansen and Ostergaard⁵ have reported experiments in which they attempted to selectively reduce NO with CH₃NH₂ and with (CH₂ NH₂)₂ at temperatures as low as 530°C. While these experiments appeared to give positive results, the experimental procedures they used would not distinguish between reducing NO to molecular nitrogen and oxidizing it to NO₂. An analogous set of experiments with N₂H₄ were done by Azuhata, Akimoto, and Hisinuma⁶ who found that NO was selectively removed at temperatures as low as 400°C. These experiments did distinguish between reduction to molecular nitrogen and oxidation to NO₂, and the latter was found to be the dominant process. The problem here is that while N₂H₄, CH₃NH₂ and (CH₂ NH₂)₂ are all capable of forming NHR radicals which might be expected to reduce NO, these radicals contain hydrogen atoms which are alpha to the free valence. It is well known in free radical chemistry that free radicals with that structure react rapidly with O₂ to form an unsaturated molecule and an HO₂ radical. The rapid reaction HO₂ + NO = NO₂ + OH would then cause the NO to disappear.

Experiments have also been done in which NH₂COOH, NH₂ SO₂ NH₂, NH₂SO₃H, C₆H₅NH₂, NH₂OH, and NH₂Cl were examined as possible selective NO reducing agents⁷.

It was found that NH₂OH reacted to produce additional NO. While hydrogen abstraction from NH₂OH can produce HNOH radicals which would be expected to reduce NO, it can also produce NH₂O radicals which would decompose to form additional NO.

NH₂COOH and NH₂Cl both showed some effectiveness for reducing NO, but were inferior to NH₃. For NH₂COOH the problem may be that, as with NH₂OH, the chemistry favors producing the wrong radical. For NH₂Cl hydrogen abstraction will form NHCl radicals which would be expected to react with NO, initially forming HCINNO molecules. While the desired reaction path, isomerization to CINNOH followed by decomposition to Cl + N₂ + OH, would provide chain branching, HCINNO may also be able to decompose to HCl and N₂O, a chain terminating process.

NH₂ SO₂ NH₂ and NH₂SO₃H by themselves showed no ability to reduce NO but did so at temperatures above 700°C in the presence of CO, i.e. with CO oxidation acting as a source of chain carriers, these molecules produces radicals that can selectively reduce NO, but that reaction does not

⁵D. Wenli, K. Dam-Johansen and K. Ostergaard 23th Symposium (International) of Combustion, 297-303 (1990)

⁶ S. Azuhata, H. Akimoto, and Y. Hisinuma, AIChE Journal, 31, 1223-1225 (1985)

⁷ R. K. Lyon, Final Report for DOE Grant DE-FG05-92ER81398, Copies available from the author upon request.

produce enough radicals for a self sustaining chain reaction.

$C_6H_5NH_2$ selectively reduced NO at temperatures as low as 400°C, but this reduction was far too slow to be practically useful. Since the hydrogen atoms on the NH_2 group in $C_6H_5NH_2$ are far more reactive than those on the ring it seems likely that forming the “wrong radical” is not the problem in this case, i.e. probably $C_6H_5NH_2$ reacts to form C_6H_5NH radicals. It also seems likely that just as NH_2 reacts with NO to form H_2NNO which isomerizes to $HNNOH$, C_6H_5NH reacts with NO to form C_6H_5NHNO which isomerizes to C_6H_5NNOH . $HNNOH$ is, however, a small molecule. When it is formed with a large amount of vibrational energy it immediately dissociates. Since C_6H_5NNOH is a much larger molecule with many more vibrational modes to soak up the excess energy with which it is formed, its dissociation will be much slower, allowing the excess energy to be lost by collisional deactivation. This would lead to a degenerate branching situation, i.e. initially the reaction between C_6H_5NH and NO removes chain carriers, but as C_6H_5NNOH accumulates, it dissociate to produce free radicals and the reduction of NO proceeds albeit at a low rate.

The Possibility of Modifying Thermal DeNOx Chemistry to suit Diesel Engines: The Use of Other Radicals NH_2 is not the only kind of radical known to be capable of reducing NO. Hydrogen abstraction from $HNCO$ can form the free radical NCO which is known to react rapidly with NO, reducing it to N_2O . The initial report of the RAPRENOx process⁸ claimed that $HNCO$ was capable of reducing NO at temperatures as low as 592°C, but subsequent work showed that reduction of NO by $HNCO$ produces much more N_2O than does the reduction with NH_3 and that the two processes have essentially identical temperature windows. Since the reaction sequence



rapidly converts $HNCO$ into NH_3 , this is not surprising.

The free radical N_3 also reacts rapidly with NO reducing it to N_2O . NaN_3 is a solid which on heating decomposes instead of melting. The initial products of this decomposition are gaseous sodium atoms and N_3 radicals with the N_3 radicals reacting with each other to form molecular nitrogen⁹. Since the reaction $N_2O + Na = N_2 + NaO$ is known to be rapid the injection of NaN_3 into hot exhaust gas might allow the rapid and selective reduction of NO to N_2 . The author has done a preliminary experiment in which NaN_3 decomposition was found to rapidly and selectively reduce NO, but the cost of NaN_3 and the handling difficulties it involves make this observation more a matter of scientific interest than of potential practical utility.

The Possibility of Modifying Thermal DeNOx Chemistry to suit Diesel Engines: The Conversion of NO to NO_2 When changing one of two reagents in a chemical reaction does not have

⁸ R. A. Perry and D. L. Siebers,, Nature, 324, 657-658 (1986)

⁹ L. G. Piper, R. H. Krech, and R. L. Taylor, J. Chem. Phys. 71, 2099 - 2104 (1979)

the desired effect, one can consider changing the other. The oxidation of methanol can be used to quantitatively convert NO to NO₂ at temperatures as low as 500°C¹⁰. Unfortunately, however, this is another case of the “wrong radical”, i.e. in NO the free valance is on the nitrogen, but in NO₂ the free valance is on the oxygen. Consequently the chief reaction of NH₂ with NO₂ is to form NO and H₂NO with the H₂NO then decomposing to additional NO, a contraproductive result.

The Possibility of Modifying Thermal DeNO_x Chemistry to suit Diesel Engines: The Use of Free Radical Sources other than Hydrogen Oxidation Reference 7 also reports a series of experiments in which materials which oxidize readily were tested as alternatives to hydrogen oxidation for promoting the Thermal DeNO_x reaction. Nothing of any great promise was found. The problem here is that it is not enough to find a reaction that provides free radical chain carriers at the roughly 500°C temperature of diesel exhaust. In addition to providing chain carriers which react with NH₃ to produce NH₂, the reaction must also avoid producing chain carriers such as HO₂ which will react with the NO to convert it to NO₂.

The Possibility of Modifying Diesel Engines to suit Thermal DeNO_x Chemistry: Definition of the Problem The use of the Thermal DeNO_x reaction to control NO_x emissions has three requirements: the gas from which NO is to be removed must be at a temperature in the 1300°F to 2000°F range, the gas's temperature must homogeneous in space and constant in time, and the gas must undergo rapid and complete mixing with the reducing agents.

The first of these requirements is obviously a problem. The Thermal DeNO_x reaction is exothermic but only weakly so. If we assume that 600 ppm NO is reduced with 900 ppm NH₃ and 1800 ppm H₂, the rest of the exhaust gas having a composition of 10% O₂, 6.9% CO₂, 6.2% H₂O, and balance nitrogen, the heat released by the reduction of the NO will provide a temperature increase of 42.5°F. While it is possible to raise the temperature of the exhaust gas by burning more fuel, the amount of fuel this requires is substantial. For an engine using a diesel fuel with an H/C ratio of 1.8, and a heat of formation of -5.5 kcal/mole of C, the additional fuel consumption needed to raise the exhaust gas temperature from 942.5°F to 1300°F, is 14.9% of the primary fuel consumption.

Since exhaust gas leaving an engine is in intensely turbulent flow, its temperature is necessarily homogeneous in space. Temperature variations with a short time constant may occur due to the cyclic nature of the combustion process in engines. Mollenhauer¹¹ has reported experimental data and calculations illustrating these rapid temperature fluctuations. Whether or not these fluctuations are a problem will depend on the manner in which the reducing agents are mixed with the exhaust gas. Temperature variations with a much longer time constant may occur due to changes in load. If, however, these variations are within the 1300°F to 2000°F range, they can be accommodated by adjusting the NH₃/H₂ ratio.

¹⁰ R. K. Lyon J. C. Kramlich, S. C. Chen, and J. A. Cole, Combust. & Flames 81, 30-39 (1990)

¹¹ K. Mollenhauer SAE paper 670929

The flow of exhaust gas pulsates strongly. Simply adding the reducing agents at a constant rate to the exhaust gas flow will put excessive reagent into some of the exhaust gas too little into other parts of it.

The Possibility of Modifying Diesel Engines to suit Thermal DeNO_x Chemistry: Available Pieces of the Puzzle Before discussing how the requirements above might be met, it is useful to provide some background material. A number of technologies which were developed for other applications are relevant to this problem.

In the 1970s the problem of controlling emissions from automobile engines (i.e. spark ignition IC engines) prompted the development of catalytic reactors and of thermal (i.e. noncatalytic) reactors. For the latter type of system NO_x emissions were kept to then acceptably low levels by operating the engine somewhat fuel rich. This produces a CO and hydrocarbon containing exhaust gas which is sent to the thermal reactor to be mixed with air and oxidized. The problem in designing the thermal reactor is the quality of the mixing that is needed. The air going into the thermal reactor is cold. If some of the exhaust gas is mixed with too much air it will not be hot enough for rapid CO oxidation. If some of the exhaust gas is mixed with too little air, i.e. with a less than stoichiometric quantity of air, the CO will not be completely oxidized. Since the amounts of CO and hydrocarbons in the exhaust gas is modest, the range between too little air and too much air is narrow. Thus the design of a thermal reactor for this application involves a mixing problem analogous to that discussed above for Thermal DeNO_x.

R. J. Lang¹² has reported a design for one of these noncatalytic reactor systems. The Lang design sends the CO containing exhaust gas through a torus shaped mixing chamber, mixing it with added air. On leaving this mixing chamber the exhaust gas air mixture travel through an insulated duct. Thus the Lang design uses a well mixed reactor followed by a plug flow reactor. This combination allowed a system small enough for use on an automobile to provide complete oxidation of CO and hydrocarbons over the full range of operating conditions after startup.¹³

The Lang design used a volume for the mixing torus that is twice the cylinder volume. In terms of the requirements for Thermal DeNO_x this is attractive since it would appear to provide both complete rapid mixing of the reducing agents with the exhaust gas and mixing of the exhaust gas with itself so as to eliminated temperature fluctuations.

Hardesty and Weinberg¹⁴ have discussed combustion systems in which there is extensive heat exchange between the fuel and air going into the combustion zone and the products of combustion coming out of it. This kind of heat exchange is used in the well known bootstrap and jellyroll combustors and in the Thermatrix system. Using a system of this kind would allow heating exhaust gas

¹² R. J. Lang, SAE paper 710608

¹³ While some CO and hydrocarbon emissions did occur during startup, it seems likely that these could have been greatly reduced by insulating the reactor internally rather than externally.

¹⁴ D. R. Hardesty and F. J. Weinberg, Comb Sci. And Tech., 8, 201-214 (1974)

to a temperature adequate for the Thermal DeNO_x reaction to occur. For the example given above and assuming that the heat exchange system operates with a ΔT of 50°C reduces the additional fuel consumption from 14.9% to 3.8%. As Page and Edgar¹⁵ have pointed out, heating and cooling the exhaust gas would have the additional benefit that it would oxidize organic particulate matter. These advantages, however, must be weighed against the capital cost of the heat transfer surface required, the added weight and volume and the added pressure drop it puts on the exhaust system. The heat exchanger is also a thermal mass, i.e. there would be a delay between starting the engine and reaching the temperature necessary for NO_x control.

The problem of providing an adequate temperature for the Thermal DeNO_x reaction changes when one considers turbocharged diesel engines, especially those which are used to generate electrical power. In most designs the turbocharger is an energy recycle device, i.e. it extracts energy from the exhaust gas as it leaves the engine and returns it to the engine as compressed combustion air. This improves fuel economy. As a result of this improvement the temperature at which the exhaust gas is discharged from the turbocharger is decreased, but the temperature of the exhaust gas as it flow out of the engine to the turbocharger is increased.

Shahed¹⁶ has described a design in which the turbocharger is not limited to recycling energy to the engine. Instead both the engine and the turbocharger can generate electricity. This allows solving a fundamental problem, the mismatch between the flow characteristic of reciprocating engines and turbochargers. At high engine speeds the turbocharger develops too much power and at low engine speeds it develops too little. If, however, the turbocharger is equipped with a motor generator, it can produce electrical power or accept it as needed. Shahed states that this approach can provide a 6% to 10% in fuel economy. While the design described by Shahed does not make the turbocharger into a net producer of electricity, it would appear possible to do so by raising the pressure at which exhaust gas leaves the engine and goes to the turbocharger. While this would decrease the engine's ability to do work it would increase the turbocharger's ability to do work. Thus it may be possible to bring the exhaust gas traveling between the engine into the Thermal DeNO_x temperature range with little or no sacrifice of overall efficiency.

¹⁵ D. Page and B. Edgar, Proceedings of the 1998 Diesel Engine Emissions reduction Workshop, Maine maritime Academy, Castine Maine, July 6-9, 1998, pp 229-235

¹⁶ S. H. Shahed, Proceedings of the 1998 Diesel Engine Emissions reduction Workshop, Maine maritime Academy, Castine Maine, July 6-9, 1998, pp143-150

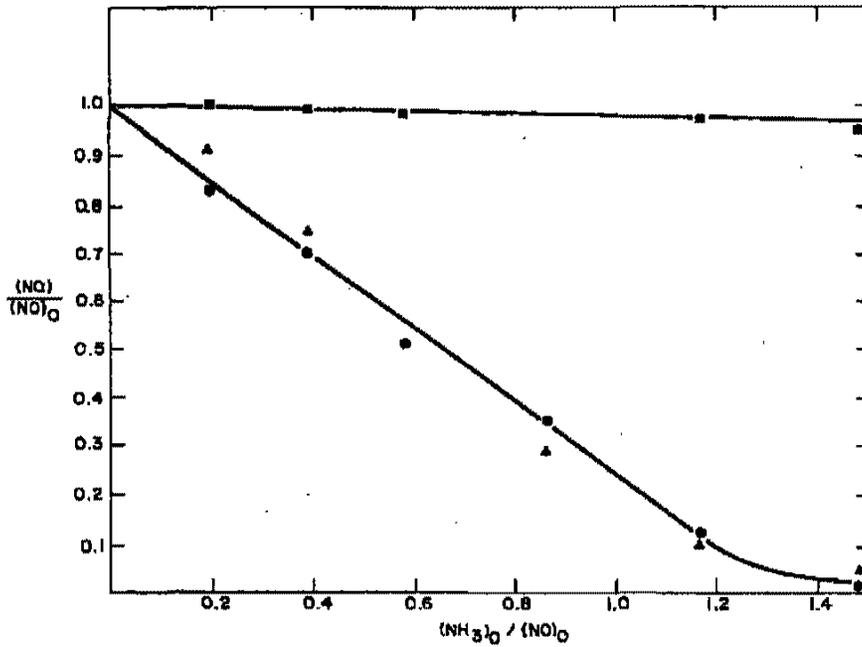


Figure 1. Reduction of NO by the NO-NH₃-O₂ reaction. T = 982°C, reaction time = 0.075 sec, [NO]₀ = 1020 ppm = 1.2 × 10⁻⁴ mole/l. ▲—O₂ = 2.2% = 2.6 × 10⁻⁴ mole/l. ●—O₂ = 0.5% = 6 × 10⁻⁵ mole/l.; ■—no O₂.

Figure 2
TEMPERATURE "WINDOW" FOR THERMAL DENO_x REACTION-H₂+NH₃

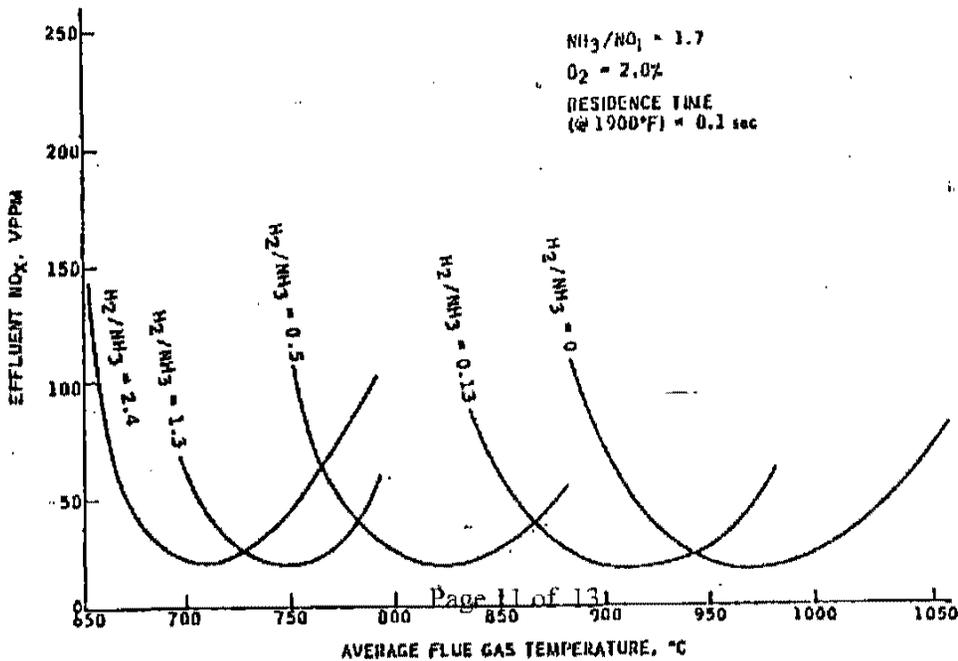
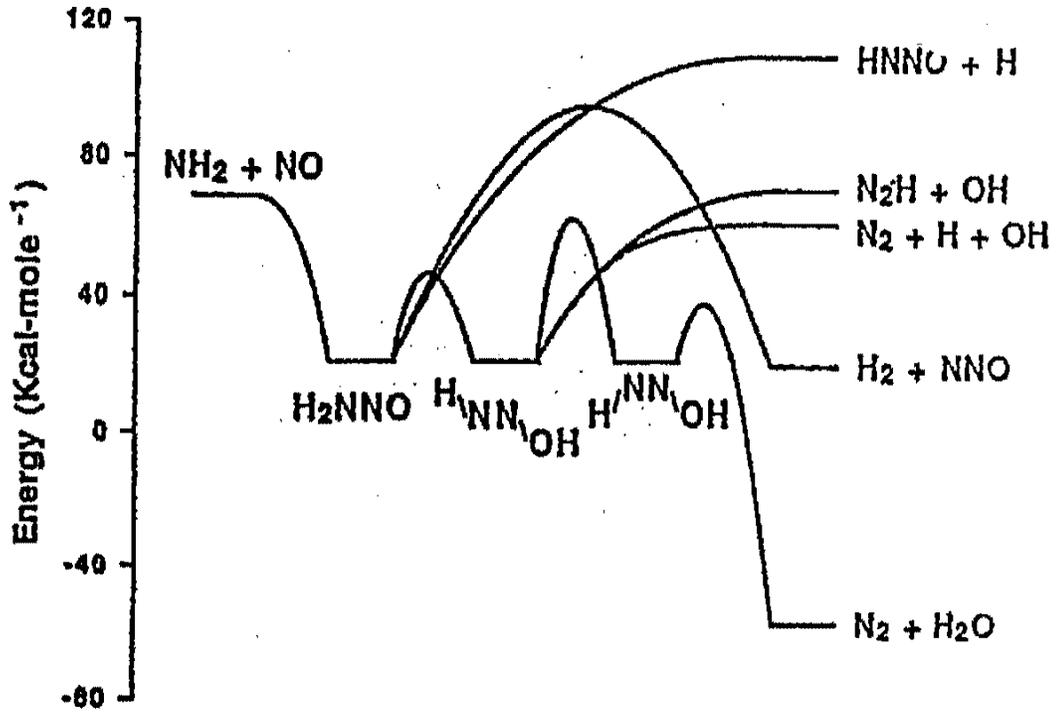


Figure 3



Reaction coordinate diagram for the reaction $\text{NH}_2 + \text{NO} \rightleftharpoons \text{products}$.

Fig. 3 - Temperatures behind the engine (measuring point 2), with a medium-size exhaust gas pipe volume