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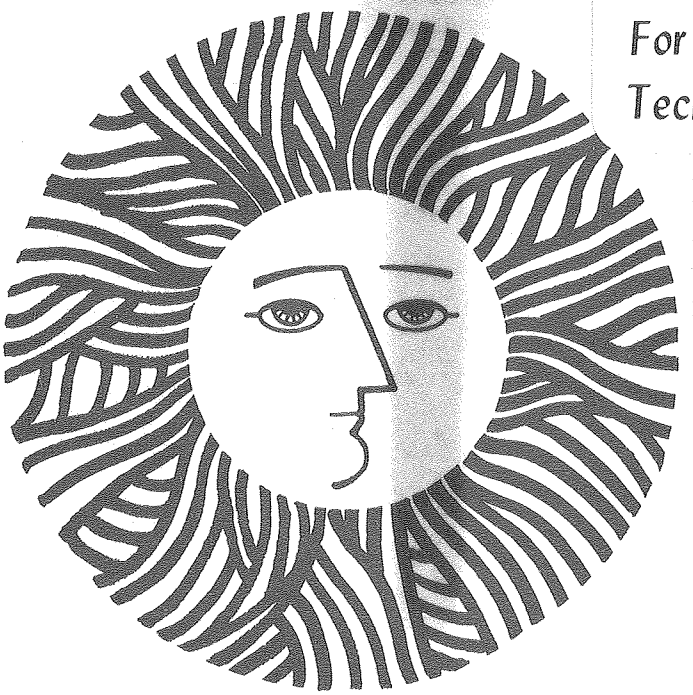

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COMBUSTION SOURCES OF NITROGEN COMPOUNDS*

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Consideration of odd-nitrogen compounds (essentially all nitrogen compounds other than N_2) as air pollutants has primarily focused upon the nitrogen oxides, NO and NO_2, with occasional interest in ammonia. The importance of odd-nitrogen compounds other than NO and NO_2 is not well understood but it is reasonable to assume that they are at least as reactive as the oxides of nitrogen and therefore should be of at least equal concern on an equal mass basis.

The combustion literature contains relatively small amounts of data on non-criteria nitrogen pollutants so that it presently is not possible to appraise their effect on air quality. The reasons for the current state of affairs are basically twofold. First, there are major sampling and analysis difficulties that must be overcome to render unambiguous quantitatively correct measurements of these compounds. Second, there is a general lack of understanding of the formation and destruction mechanisms of these compounds in combustion mixtures, and these are prerequisite for establishing the specific compounds to be measured and provide restrictions on the techniques used.

This communication describes some combustion sources of non-criteria nitrogeneous pollutants. Thermal and fuel-nitrogen production of NO are briefly described. The role of the automobile in the production of non-criteria nitrogen pollutants is summarized, and this is followed with a brief mention of non-criteria emissions from aircraft. The paper is concluded with a brief discussion of the possible production of nitrogen compounds from the application of currently accepted abatement technology.

The review makes no pretense of providing a complete description of the non-criteria nitrogen pollutant problem, but rather attempts to provide the reader with a broad overview of potential problem areas.

One of the major sources of nitrogen emissions from combustion systems results from the oxidation of atmospheric molecular nitrogen to NO and this is referred to as thermal NO. The formation mechanism of thermal NO in lean and near-stoichiometric combustion is reasonably well-understood; however the formation mechanism of NO in rich combustion systems is not firmly established. Recent evidence suggests that hydrocarbon chemistry and nitrogen oxide formation chemistry are coupled and that nitrogen containing radical species are involved in nitrogen oxide production.

The second major source of combustion generated nitrogen compounds results from nitrogen chemically bound to fuel species. Nitric oxide produced from the nitrogen contained in fuel molecules is referred to as fuel NO. Table 1 lists the typical nitrogen content of common hydrocarbon fuels. Elemental analysis of these fuels is performed with relative ease; however, data are lacking on the specific identities of the various nitrogen compounds in the fuels. The small number of pyrolysis studies performed on real fuels has indicated that the nitrogen containing gas phase pyrolysis compounds are rather simple low molecular weight species.

Until recently thermal NO has been the dominant source of NO; however, in combustion processes using crude oil, coal and shale derived fuels, and some refinery gases, fuel nitrogen can be a significant and even dominant source of NO. The amount of fuel nitrogen NO produced in combustion processes increases with nitrogen content of the fuel.

TABLE 1

Typical Nitrogen Content of Fuels

Fuel	Ave. Nitrogen (wt. %)	Range	Reference
Crude Oil	0.65		Ball and Roll (1962)
Asphaltine	2.3		Ball and Roll (1962)
Light Distillate Oil	0.07	0-0.6	Ball and Roll (1962)
Heavy Distillate Oil	1.4	0.6-2.15	Ball and Roll (1962)
U.S. Crude		.06-.49	Sarofim and Flagan (1976)
Shale Derived Heavy Oil	1.4		Heap (1978)
Coal	1.4		Sarofim and Flagan (1976)
Coal Liquids		0.3-0.5	Heap (1978)
Coal-oil Slurry	0.65		Heap (1978)

Nitric oxide production from fuel nitrogen has been the object of much recent study. The detailed chemical mechanism of NO production from fuel nitrogen remains unknown, and the product nitrogen species, in most studies, have neither been all identified nor measured quantitatively. Some general trends emerge when one reviews the extensive literature associated with premixed combustion studies of fuel nitrogen oxidation and these are:

a) NO formation rates appear to be on the same time scale as hydrocarbon reactions.

b) The NO concentrations in the flame zone exceed the post flame NO concentrations.

c) In the post combustion zone relative to the combustion zone, the NO concentration decreases relatively slowly for fuel lean flames and more rapidly for fuel rich flames.

d) NO yields are sensitive to the fuel/air equivalence ratio with lean and near stoichiometric flames resulting in high yields and rich flames resulting in low yields.

e) In contrast to thermal NO yields the fuel NO yields are not strongly temperature dependent.

It is crucially important to account fully for the fate of the fuel nitrogen in combustion processes, particularly for the fuel rich case where yields are smaller.

The automobile appears to be a potential source of non-criteria nitrogen pollutants which should be investigated further. A few illustrative examples of research performed in the area of automotive combustion will be given in subsequent paragraphs.

Seizinger and Dimitriades (1972) analyzed exhaust gases from an automobile using simple hydrocarbon fuels using GC/MS techniques. Nitroalkanes were found (with the most abundant species being nitromethane) present in variable amounts between 0.8 and 5.0 ppm. Schuchmann and Laidler (1972) performed model pyrolysis studies of ethane and acetaldehyde in the presence of nitric oxide in the temperature range 770-870K. Various nitrogen compounds including nitriles and amines were identified in the products. They also analyzed the exhaust gases of a 1963 automobile under slightly fuel rich and rich conditions and found that ammonia and low molecular weight amines were present. Schuchmann and Laidler suggest that nitrogen compounds other than oxides and molecular nitrogen are likely to be present in the exhaust gases from internal combustion engines operating under a variety of fuel rich conditions.

Hum et al. (1974, 1976) sampled the exhaust gases of three 1972 vehicles and two stationary engines. Concentrations of 1 to 1.5 ppm HCN were detected and nitromethane was also measured. These investigators suggested that ammonia was also present, although this was not confirmed experimentally

Other nitrogen compounds which have been identified in automobile exhausts are nitriles, alkyl-nitrates, nitro-alkanes and alkenes, and alkyl amines. These compounds are difficult to measure; however a preliminary attempt at providing data has indicated the presence of enough undesirable species to suggest that further study is required. In contrast, relatively little work has been performed on the characterization of non-criteria emissions from compression ignition (diesel) engines.

The gas turbine engine which is used extensively in aircraft is another source of non-criteria nitrogen emissions. Significant concentrations of NO_2 have been measured in gas turbine exhausts. The effect of forming NO_2 during combustion rather than forming it entirely in the atmosphere would be to decrease the induction period for photochemical smog formation. There is concern that the measured NO_2 concentrations in the exhaust are not characteristic of the source emissions and result, instead, from unsatisfactory measurement techniques. Comparative measurements of NO_2 using a variety of techniques under identical conditions are required to clarify whether NO_2 is present in the combustion system or whether the indicated concentrations are artifacts of the analytical techniques.

Stumpf and Blazowski (1976) describe a multi-organizational study of aircraft exhausts using a variety of operating conditions and fuel types. A simulated alternative fuel blend with 25 percent aromatics and increased nitrogen content (controlled by pyridine doping) resulted in increased exhaust aromatics and increased nitrogen containing organic species over normal JP4 type fuels.

In another study of aircraft exhaust composition, Conkles et al. (1976) used GC/MS analysis to measure trace organic compounds in aircraft turbine combustor exhaust as a function of fuel type and engine operating conditions. Nitriles, nitro-alkanes, heterocyclic compounds and nitrates were found in the combustion products of ordinary JP4 fuel; however, increased organic nitrogen emissions were found in fuels containing chemically bound nitrogen.

Power plants are an additional source of non-criteria nitrogeneous pollutants. The transition from natural gas to heavier fossil fuels is likely to have a substantial environmental impact. Pierotti and Rasmussen (1976) have recently measured N_2O in the stack gases from facilities burning coal and natural gas. N_2O concentrations between 3.1 and 11.0 ppm were noted for the plants operating on natural gas; however, N_2O emissions from coal burning plants were an order of magnitude higher. Since power plants utilize lean combustion and boilers have characteristically long residence times in the high temperature portion of the power generation portion of the cycle, the non-criteria pollutants produced (except for N_2O) should be minimized during operations at optimum conditions. The fate of the chemically bound nitrogen should be resolved for probable rich off-design operations.

Ironically, many air pollution control strategies which are directed at satisfying NO_x emissions regulations may inadvertently promote the production of unregulated nitrogen pollutants. A brief mention of some control strategies and potential problems that may be associated with them will be given in subsequent paragraphs.

Exhaust purification catalysts are widely used to promote oxidation of CO and unburned hydrocarbons. The catalysts are designed to operate under oxidizing conditions. Voorhoeve et al. (1975) showed that HCN formation (i.e. up to 80 ppm with water present

and 700 ppm without H_2O) over Pt under reducing conditions appear possible in automotive catalytic exhaust systems where there is a low air/fuel ratio. Such conditions are possible in deceleration modes and downhill coasting. Subsequent studies by Bradow and Stump (1977) confirmed the production of HCN over Pt-Rh and Pt-Pd automotive catalyst. Their studies also indicated that fuel sulfur in gasoline which forms SO_2 inhibits the HCN formation. Voorhoeve et al. (1978) in a recent investigation regarding the inhibitory effect of SO_2 on HCN formation concluded that intermittent admission of O_2 over a Pt catalyst may maintain the catalyst in a state where it is possible to produce HCN even if SO_2 is present in the gas mixture. In automotive exhaust systems intermittent admission of O_2 occurs during lean operation.

Staged combustion is a method of combining fuel rich and lean combustion to stabilize an overall fuel lean process. NO production is inhibited in the first stage due to lack of available oxygen. The partially oxidized products of the first stage are delivered to the second stage, mixed with air and the combustion process is completed. The low temperatures associated with the second stage inhibit the production of thermal NO . It is not clear how this process works with regard to fuel nitrogen. The fuel nitrogen is likely to be pyrolyzed to a low molecular weight nitrogen compound which is reduced during the first stage. If the first stage reduced nitrogen compound is molecular nitrogen, the overall process should behave similarly with regard to thermal and fuel NO_x. It is not obvious that this is the case. It is important to determine the fate of the fuel nitrogen in model systems, and to analyze for non-criteria nitrogen species in second stage exhaust gases.

A new method of controlling NO_x has been patented by Exxon Research and Engineering Company which selectively removes NO from combustion effluents through homogeneous reaction with ammonia and oxygen. This process is distinctly different from other technologies in that it removes NO after its formation rather than attempting to prevent its formation. Thus, the process offers the possibility of removing both thermal and fuel NO . This process has been demonstrated commercially in Japan and is likely to be proposed for use in California for the control of oxides of nitrogen from stationary sources. A major question regarding this process is its potential for formation of secondary pollutants, especially at operating conditions different from those which are optimal for the reduction of oxides of nitrogen.

As additional analytical methods become available and more insight is gained regarding nitrogen compound formation and destruction mechanisms in combustion processes, better data associated with non-criteria nitrogen species will become available. These will be useful in assessing the hazards of non-criteria nitrogen compound emissions. This information will also be useful to technologists concerned with the design and implementation of control strategies.

REFERENCES

Ball, J.S. and Roll, H.T. (1962). Nonhydrocarbon compounds of a California petroleum. Presented at the 27th Midyear Meeting of the API Refinery Division, San Francisco, California.

Bradow, R.L., and Stump, F.D. (1977). SAE (Society of Automotive Engineers) Technical Paper No. 770367, Warrendale, Pennsylvania.

Conkles, J.P., Lackey, W.W., Martin, C.L. and Miller, R.L. (1976). Organic compounds in turbine combustor exhausts. International Conference on the Sensing of Environmental Pollutants, Las Vegas, Nevada, Paper No. 27-2.

Heap, M.P. (1978). Use of alternative fuels in stationary combustors, Progress in Astronautics and Aeronautics 62, 116.

Hurn, R.W., Allsup, J.R. and Cox, F.W. (1974). Effect of gasoline additives on gaseous emissions. EPA Report No. EPA-650/2-75-014.

Hurn, R.W., Cox, F.W., and Allsup, J.R. (1976). Effect of gasoline additives on gaseous emissions, Part II. EPA Report No. EPA-600/2-76-026.

Pierotti, D. and Rasmussen, R.A. (1976). Combustion as a source of nitrous oxide in the atmosphere. Geophysical Research Letters 3, 5, 265-267.

Sarofim, A.F. and Flagan, R.C. (1976). NO_x control for stationary combustion sources. Prog. Energy Comb. Sci. 2, 1-25.

Schuchmann, H.P. and Laidler, K.J. (1972). Nitrogen compounds other than NO in automobile exhaust gas. J. APCA 22, 1, 52.

Seizinger, D.E. and Dimitriades, B. (1972). Oxygenates in exhaust from simple hydrocarbon fuels. J. APCA 22, 1, 47-51.

Stumpf, S.A. and Blazowski, W.S. (1976). Detailed investigations of organic compound emissions from aircraft gas turbine engines. Paper No. 27-1. International Conference on the Sensing of Environmental Pollutants. Las Vegas, Nevada.

Voorhoeve, R.J.H., Patel, C.K.N., Trimble, L.E. and Kerl, R.J. (1975). Hydrogen cyanide production during reduction of nitric oxide over platinum catalysts. Science 190, No. 4210, 149.

Voorhoeve, R.J.H. (1978). Hydrogen cyanide production during reduction of nitric oxide over platinum catalysts: transient effects. Science 200, May 1978.

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