



Project Summary

Effect of Fuel Sulfur on Nitrogen Oxide Formation in Combustion Processes

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Because chemically bound nitrogen in fossil fuels has been shown to be an important contributor to nitrogen oxide (NO_x) emissions, much research has been focused on mechanisms governing the oxidation of fuel nitrogen to fuel NO. This has been done, hoping that the insight and understanding gained thereby will lead to development of new combustion modifications for NO_x control. However, many fuels containing chemically bound nitrogen also contain sulfur in various amounts. Indeed, insofar as pulverized coal is concerned, a wide variation in sulfur content is possible, even from coals with similar nitrogen contents. The question can, therefore, be posed, is the sulfur content of a fuel likely to have a major influence on the resulting NO_x emissions? Specifically, will the presence of fuel sulfur cause major changes in mechanisms of fuel NO formation? Furthermore, since there exist a wide variety of possible combustion conditions and combustion modifications, it is to be expected that the potential importance of SO_x/NO_x interactions depends not only on the fuel quality, but also on the conditions under which the fuel is burned.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of

the same title (see Project Report ordering information at back).

Introduction

This report describes results of a far ranging study to determine: (1) if sulfur has a measurable effect on fuel nitrogen conversion in practical combustion configurations, and (2) the mechanisms through which this effect, if it exists, is implemented. Results from the practical turbulent diffusion flame studies did in fact indicate that sulfur may have a first order influence on fuel NO emissions when the fuel is burned under hot, poorly mixed combustion conditions in which fuel nitrogen processing occurs in long-lived, hot rich zones. These results, which are of practical significance, prompted further studies on fuel nitrogen processing in hot, rich, premixed, laminar flame environments.

The project was divided into four phases:

1. Fuel sulfur effects on NO_x formation in turbulent diffusion flames.
2. Interactions of fuel sulfur and fuel nitrogen in fuel-rich premixed laminar flames.
3. Post-flame behavior of nitrogenous species in the presence of fuel sulfur (rich, moist $\text{CO}/\text{Ar}/\text{O}_2$ flames)
4. Post-flame behavior of nitrogenous species in the presence of fuel sulfur (rich, moist $\text{CH}_4/\text{He}/\text{O}_2$ flames)

Each phase logically followed the previous one and originated from the need to obtain more fundamental data to understand and generalize the effects observed. Phase 1 was concerned only with exhaust NO measurements; Phase 2

with NO profiles; Phase 3 with NO, HCN, NH₃, and N₂ profiles in CO flames and their kinetic modeling; and Phase 4 with profiles of the same species in CH₄ flames.

Phase 1: Turbulent Diffusion Flames

Interactions between certain fuel sulfur compounds and nitric oxide (NO) in turbulent gaseous and distillate oil diffusion flames were experimentally investigated in a 75,000 Btu/hr (22 kW) laboratory combustor. Aerodynamic, air preheated conditions, and overall excess air conditions were varied to determine their role in any such interaction.

Results indicated that adding sulfur dioxide (SO₂) to natural gas flames could enhance or inhibit NO emissions. Local flame stoichiometry and temperature, which were influenced by fuel injector type, determined which effect was observed and the extent to which it occurred. Thiophene (C₄H₄S) and pyridine (C₅H₅N) were added to No. 2 diesel oil to determine effects of fuel sulfur on conversion of chemically bound fuel nitrogen to NO. No discernible effect was observed at "zero" air preheat conditions. No emissions were enhanced at high air preheat conditions. Adding SO₂ to natural gas flames doped with ammonia (NH₃) significantly increased the conversion of NH₃ to NO at high air preheat conditions.

Inhibition effects were explained in terms of homogeneous catalysis of recombination reactions by SO₂. Hydrogen abstraction reactions involving reduced form were considered to explain the enhancement effect.

Phase 2 : No Profiles in Premixed Laminar Flames

Significant fuel sulfur and fuel nitrogen interactions were observed in the post-reaction zone of premixed flat flames. Methane/oxygen/argon flames of stoichiometric ratios between 0.40 ($\phi = 2.5$) and 1.2 ($\phi = 0.833$) were doped with cyanogen and with sulfur additives (SO₂ and H₂S). The resulting profiles of NO in fuel-rich studies exhibited an enhancement of peak NO formation due to sulfur species. These peak NO values decayed rapidly in the later portions of the flame, indicating the continuation of low temperature (below 1600 K) reactions. In some instances, the presence of sulfur species cause the decay or reduction of NO to proceed

below the base line values at very long (greater than 0.1 sec) residence times.

Phase 3: Nitrogenous Species Profiles in CO Flames

Experimental measurements of NO, N₂, and other nitrogenous species in the post-flame gases of rich ($\phi = 2.17$) premixed laminar CO/Ar/O₂ (trace H₂) flames, with fuel nitrogen as NO, C₂N₂, and NH₃, and fuel sulfur as SO₂, allowed the nitrogen balance to be closed to within 7%. In the absence of hydrocarbons and with only a trace of hydrogen, NO decayed homogeneously to form N₂ at high temperatures, and the fate of the fuel nitrogen was independent of the type of fuel nitrogen species. The effect of fuel sulfur was to decrease post-flame NO levels and increase N₂ more rapidly. The observed decay in NO and formation of N₂ were consistent with detailed kinetic calculations employing only the reverse Zeldovich mechanisms to form N and N₂. There was no evidence of other N₂ formation mechanisms being important for these hydrogen-poor flames, at either high or low temperatures. Calculations also showed that the most plausible effect of SO₂ in the mixture was to increase the steady state N atom concentration through direct interactions between N, NO, S, and SO.

Phase 4: Nitrogenous Species Profiles in CH₄ Flames

Profiles of NH₃, HCN, NO, and N₂ in premixed CH₄/He/O₂/C₂N₂ flames allowed the nitrogen balance to be closed to within 3% in the far post-flame region of rich flames at stoichiometric ratios greater than 0.58 ($\phi < 1.72$). In the flame front and the near post-flame, a (decaying) discrepancy in the nitrogen balance was attributed to N₂ which was being destroyed to form N₂. For exceedingly rich sooting flames (SR=0.46, $\phi = 2.17$), closure was impossible due to nitrogenous species adsorbed on solid particles. In all cases the effect of sulfur was to increase the sum of NO + HCN + NH₃ and to decrease N₂. This is consistent with previous data on hydrocarbon flames. Results showed that sulfur accelerates hydrocarbon decay rates, thereby inhibiting hydrocarbon breakthrough, which apparently influences the XN species profiles in the post-flame. Certainly, hydrocarbons and possibly hydrogen play a critical role in the enhancement effect that fuel sulfur has on fuel nitrogen conversion.

Conclusions

Results from this project, taken as a whole, indicate that, under hot rich conditions often considered optimum for NO abatement by staged combustion fuel sulfur tends to increase the conversion of fuel nitrogen in hydrocarbon fuels.



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The complete report, entitled "Effect of Fuel Sulfur on Nitrogen Oxide Formation in Combustion Processes," (Order No. PB 88-208 178/AS; Cost: \$25.95, subject to change) will be available only from:

National Technical Information Service

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The EPA Project Officer can be contacted at:

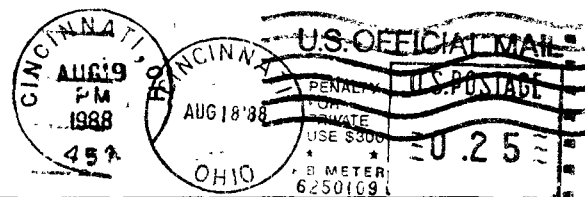
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