REAPPLICATION OF ENERGETIC MATERIALS AS FUELS

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ABSTRACT

This investigation addresses the combustion-related aspects of the reapplication of energetic materials as
fuels in boilers as an economically viable and environmentally acceptable use of excess energetic materials.
The economics of this approach indicate that the revenues from power generation and chemical recovery
approximately equal the costs of boiler modification and changes in operation. The primary tradeoff is the
cost of desensitizing the fuels against the cost of open burn/open detonation (OB/OD) or other disposal
techniques.

Two principal combustion-related obstacles to the use of energetic-material-derived fuels are NOₓ
generation and the behavior of metals. NOₓ measurements obtained in this investigation indicate that the
nitrated components (nitrocellulose, nitroglycerin, etc.) of energetic materials decompose with NOₓ as the
primary product. This can lead to high uncontrolled NOₓ levels (as high as 2600 ppm on a 3% O₂ basis
for a 5% blend of energetic material in the fuel). NOₓ levels are sensitive to local stoichiometry and
temperature. The observed trends resemble those common during the combustion of other nitrogen-
containing fuels. Implications for NOₓ control strategies are discussed. The behavior of inorganic
components in energetic materials tested in this investigation could lead to boiler maintenance problems
such as deposition, grate failure, and bed agglomeration. The root cause of the problem is the potentially
extreme temperature generated during metal combustion. Implications for furnace selection and operation
are discussed.

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ABSTRACT

This investigation addresses the combustion-related aspects of the reapplication of energetic materials as fuels in boilers as an economically viable and environmentally acceptable use of excess energetic materials. The economics of this approach indicate that the revenues from power generation and chemical recovery approximately equal the costs of boiler modification and changes in operation. The primary tradeoff is the cost of desensitizing the fuels against the cost of open burn/open detonation (OB/OD) or other disposal techniques.

Two principal combustion-related obstacles to the use of energetic-material-derived fuels are NO\textsubscript{X} generation and the behavior of metals. NO\textsubscript{X} measurements obtained in this investigation indicate that the nitrated components (nitrocellulose, nitroglycerin, etc.) of energetic materials decompose with NO\textsubscript{X} as the primary product. This can lead to high uncontrolled NO\textsubscript{X} levels (as high as 2600 ppm on a 3% O\textsubscript{2} basis for a 5% blend of energetic material in the fuel). NO\textsubscript{X} levels are sensitive to local stoichiometry and temperature. The observed trends resemble those common during the combustion of other nitrogen-containing fuels. Implications for NO\textsubscript{X} control strategies are discussed. The behavior of inorganic components in energetic materials tested in this investigation could lead to boiler maintenance problems such as deposition, grate failure, and bed agglomeration. The root cause of the problem is the potentially extreme temperature generated during metal combustion. Implications for furnace selection and operation are discussed.

INTRODUCTION

Significant amounts of energetic material (EM) await reapplication or reuse in the US and abroad. The institutions primarily responsible for this material include US DoD, US DOE, NASA, US DOT (Coast Guard), explosives and propellant manufacturing companies, and corresponding institutions in countries other than the US. The sources of this material include reduction of weapon inventories (conventional and nuclear) and manufacturing waste. Definitive estimates of the total amount of material are not available, but our estimate is that the US DOE material awaiting disposition is 3 million kg and growing at a rate of 50,000 kg/yr. The material for which the DoD has responsibility is estimated at 376 million kg, growing at a rate of 73 million kg/yr. In addition to logistic problems caused by this stockpile, compliance and negotiations of arms control agreements with the States of the former Soviet Union are currently being affected by lack of an appropriate means for EM reapplication. Environmentally acceptable means of disposing of this material have not yet been identified.

Because of public and regulatory concerns, open burning and detonation of these materials is becoming increasingly less acceptable. Since disposal costs are approaching $2000 per metric ton, reapplication of this material in a manner avoiding disposal fees is highly desirable. Potential reapplication technologies include use as explosives in mining and excavation and processing to withdraw high-value commercial chemicals. Some of these processes result in byproducts that could be used as boiler fuels. In addition, the EM can be converted entirely to boiler fuel by desensitization processes. Such fuels are hereafter referred to as EM-derived fuel (EMDF). The focus of this investigation is co-firing EMDF with coal,

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biomass, or other fuels in boilers or industrial furnaces. Recent economic analyses indicate that such a process could compete with open burning and open detonation if the cost of preparing EMDF can be held below the cost of open burning or open detonation. Revenues from chemical recovery and power generation approximately equal costs of boiler modifications and maintenance of new fuel feedlines [Shah, 1994]. Many of these facilities are designed to burn a wide variety of materials such as grasses, agricultural wastes, urban wood waste, and coal, and have feed systems that accommodate wide fluctuations in fuel composition and morphology. Much of the EMDF of interest could be handled in these facilities at much lower cost than current disposal processes and in a more environmentally benign fashion than either open burning or open detonation. Establishing the reapplication of energetic materials as fuels as a viable technology option depends in large measure on characterizing the fuels and their combustion properties, which is the focus of this investigation.

**FUELS AND FACILITIES**

EMDF describes two types of materials produced by established industrial processes and distinguished largely by the energetic material from which they are derived. All of the materials are rendered nonexplosive, and are characterized by transportation and storage hazards similar to traditional fuels, before being classified as EMDF. EMDF samples formed from double-base propellants or primary explosives (Hazard Class 1.1) investigated in this project are generated in an industrial (Alliant Techsystems Inc.) process that results in an emulsion of water (=30%), kerosene (=65%), and energetic material (=5%). EMDF from propellant (Hazard Class 1.3) materials is derived from industrially treated rocket motor propellant (Thiokol) as moist, porous rubber (polybutadiene) with imbedded aluminum and small amounts of residual ammonium perchlorate. Both forms of EMDF have little in common with the materials from which they are derived. The properties of these fuels are discussed separately.

![Typical Forms of Fuel Nitrogen](image)

**Primary Explosives and Double-Base Propellants**

Some potential combustion issues associated with these materials can be appreciated by examining their chemical structures, as are illustrated in Fig. 1. The materials for which data are later presented include emulsions of nitroglycerin and nitrocellulose, both of which are illustrated in the figure. The forms of nitrogen in explosives or double-base propellants (Hazard Class 1.1 materials) are predominately either nitrate groups or in physical proximity to nitrate groups. This contrasts with nitrogen in traditional fuels, which is dominated by pyrrole and pyridinic nitrogen in coal, for example, (also illustrated in the figure). The tendency for EMDF to form NOₓ will be shown to be much higher for EMDF than for traditional fuels, and these chemical differences are believed to be the primary cause of the observed differences in effluent NOₓ concentrations.

A second major difference in the chemical structures of explosive and double-base propellant EMs compared with traditional fuels is the high oxygen concentration of the former. These high oxygen contents affect important combustion properties such as heating value (Fig. 2), amount of required excess air, and stability/storage. The heating value results could be misleading. Standardized heating value analyses are based on energy content of the fully oxidized material per unit mass of fuel. In the case of EM, most of the oxidizer is contained in the sample. A more insightful comparison would be to normalize
everything by the mass of fuel plus oxidizer. Assuming air is used as the oxidizer, the values for oil and coal are approximately 2.6 and 1.8 MJ/kg, respectively, whereas TNT and RDX are approximately 3 and 5 MJ/kg, respectively. However, the EMDFs are blended with other fuels or are chemically altered so as to produce more stable materials. In addition, EMDF use is envisioned as a component (≈ 10%) of a feed stream containing predominately traditional fuels. In general, the EMDFs potentially contribute as much or slightly more energy to a combustion system as traditional fuels.

**Rocket Motor Propellant Binder**

A second major class of fuel is derived from processed rocket motors. These typically are obtained from ammonium-perchlorate-based propellant binders. After ammonium perchlorate (AP) is extracted through water washing, the residual binder is used as a fuel. The binder is typically polybutadiene, often with as much as 65% aluminum imbedded in the form of 30 μm or smaller particles. Residual AP in the fuel is less than 10%, with 3% being a representative amount. The fuel also retains significant (= 25%) moisture from the washout process. The primary combustion issues associated with this fuel include pollutant formation and the behavior of the aluminum.

In comparison to the double-base materials, NOₓ emissions from this fuel are expected to be lower and to arise less from fuel NOₓ mechanisms and more by thermal and prompt mechanisms. The only nitrogen in the fuel is from the residual AP, which would amount to less than 0.4% N in a typical formulation (3% AP residual in fuel) as opposed to ≈ 1-2% N in double-base materials (5% EM in emulsion). The nitrogen present also is less likely to form NOₓ because of its chemical form.

The behavior of the aluminum in the fuel poses a potential equipment problem. Aluminum melts at a relatively low temperature (660 °C) and burns at potentially high temperatures (adiabatic flame temperature > 3000 °C), typically established in practice by mass transfer limitations and gas dissociation. These characteristics illustrate the potential for molten aluminum forming ash deposits or oxidizing aluminum damaging components of a boiler due to the extreme temperature.

**Combustion Facilities**

Most of the data reported herein were collected from Sandia’s Multifuel Combustor (MFC), illustrated in Fig. 3. The MFC is a two-story, small pilot-scale (=100,000 Btu/hr, depending on fuel type) facility that simulates the local environment to which fuel particles are exposed as they pass through a commercial-scale, entrained-flow combustion system. Fuel is inserted through any of a series of ports along the length of the combustor, allowing variation of residence time from a few milliseconds to 4-5 seconds. The combustor wall temperature in each of the modular sections is independently controllable up to 1400 °C in sustained tests. The MFC allows experiments to be performed under well-known and well-controlled conditions while simulating most of the important characteristics of commercial-scale boilers fired with solid, liquid, or gaseous fuels. Particle and gas residence times, temperature histories, and local stoichiometry histories are independently controllable in the MFC.

In addition, experiments were conducted on a low-density mat of alumina fibers suspended in a laminar flow of combustion gases in Sandia’s Char Combustion Laboratory (CCL) in the captive particle imaging
system. This system monitors individual particle behavior for particles at least 80 μm in diameter. Particle temperature is also monitored throughout the particle combustion history.

RESULTS AND DISCUSSION

Figure 4 summarizes NOx data for the double-base EMDF under different operating conditions and as a function of exit O2 concentration. Data from samples of the emulsion containing EM are compared with data from identically prepared material without EM. The base case (without EM) indicates less than 20 ppmv NOx under all conditions. The EMDF comprises 5% of a mixture of nitroglycerin and nitrocellulose in 64% kerosene, 35% water, and 1% surfactant. It was fired at two different combustion air to atomizing air ratios, as indicated. NOx samples were collected after complete combustion and about 1.9 s gas residence time at a temperature of 800 °C at the collection point. Data are shown as measured (solid symbols) and on a 3% oxygen basis (open symbols).

The data indicate high NOx emissions, as expected, with NOx decreasing with increasing atomizing air flowrates. The trends are consistent with NOx chemistry [Bowman, 1991], but the magnitudes provide interesting contrast to traditional flames. The increase in observed NOx concentrations with the inclusion of energetic material in the emulsion attests to the efficient conversion of EM-bound nitrogen to NOx. These data represent total NOx measurements. Our measurements of NO2 vs NO indicate that at this temperature the NO accounts for over 90% of total NOx.

Figure 5 illustrates similar data for the polybutadiene material mixed with coal at a 65:35 mass ratio. In this mixture, total fuel nitrogen originates approximately 50% from the coal and 50% from the binder. In its raw form, the binder material is a porous, adherent, rubber material that is exceptionally difficult to handle. It cannot be maintained at reasonably small particle sizes without coating it with a powder or similar material to prevent reagglomeration.

Observed NOx concentrations are much
lower as compared to double-base material (Fig. 4), consistent with the lower nitrogen content of the fuel and the mode of occurrence of nitrogen. An interesting observation is that the NO\textsubscript{x} levels observed for the double-base material exceed equilibrium NO\textsubscript{x} at the prevailing oxygen concentrations even at the highest anticipated flame temperatures (1400 °C) of the system. This suggests that the decomposition of the energetic material proceeds through a primary product of NO\textsubscript{x}, creating super-equilibrium concentrations of NO throughout the flame. This is in contrast to traditional flames, where NO\textsubscript{x} concentrations are below their equilibrium values in the early stages of flame development and in the flame front itself. The NO\textsubscript{x} data from the binder appear much more consistent with traditional fuel behavior [Bowman, 1992].

Experiments in both the MFC and the CCL indicate that aluminum particle temperatures are exceptionally high under typical combustion conditions. In the CPI, temperatures are measured optically and calibrated with a blackbody system. The highest temperature we could achieve in the blackbody was 1700 °C, establishing the high limit of our temperature monitoring capability. Experiments were conducted in environments with oxygen concentrations ranging from 1% O\textsubscript{2} to 20% O\textsubscript{2}. Under all conditions, the particle temperature exceeded the upper limit of our diagnostic. During 12% O\textsubscript{2} experiments in the CPI, the particles melted through the alumina mat used to hold them. The Al\textsubscript{2}O\textsubscript{3} melting point is approximately 2000 °C, depending on crystalline structure. At 6% O\textsubscript{2}, the temperature was again higher than 1700 °C, but the particles did not melt through the mat. Coating of particles with coal reduced their temperatures, but never below 1700 °C. Observations at the remaining oxygen concentrations were made in the MFC and particle temperatures were very high judging from particle emission, but particles were not stationary during individual shutter cycles so no reliable temperature estimate could be made. These high temperatures are believed to induce significant NO\textsubscript{x} formation through thermal and prompt mechanisms. The precise fraction of the NO\textsubscript{x} recorded in Fig. 5 associated with non-fuel NO\textsubscript{x} is difficult to determine.

The MFC results also indicated that molten aluminum particles exist in flows well after 1.5 s of residence time. This sustained presence of molten material presents some deposition threat to the system. In addition, the large amount of inorganic material in the fuel (60% aluminum by weight) could overwhelm particulate cleanup systems if a high percentage of EMDF were fired in a boiler.

NO\textsubscript{x} emissions from energetic materials and the potential for particle deposition and damage to grates or other equipment from aluminum are genuine concerns in the reapplication of energetic materials as fuels, but both issues can be managed by blending the EMDF with other fuels and by judiciously choosing the boiler design and operating conditions with which to treat the material. In particular, NO\textsubscript{x} emissions in a 10% blend of EMDF with traditional fuel would be treatable using existing technology on many biomass and coal boilers, ammonia injection being the most common. It is not clear that NO\textsubscript{x} emissions would be as controllable using low NO\textsubscript{x} burners as with coal since the data suggest that the nitrogen quantitatively converts to NO during thermal decomposition. If this is the case, the greatest reduction would be achieved by accelerating the NO\textsubscript{x} reduction kinetics in and near the flame. Aluminum-containing fuels may best be used in entrained-flow facilities rather than on grates due to their extremely high combustion temperatures. However, the difficulty of reducing the particle size to entrainable values complicates its use in entrained
flow systems. The ash formed after complete combustion is benign and should not pose a problem for any combustor except for its quantity.

CONCLUSIONS

The potential for reapplication of excess energetic materials as boiler fuels has been economically and experimentally explored. The economics suggest that the cost of such disposal techniques could be approximately equivalent to the cost of constructing and operating the facility that removes the material and desensitizes it. Revenues gained from power generation and chemical recovery are approximately equal to expenses of boiler modifications and operation of new feedlines.

Combustion issues include the formation of pollutants, especially NOX, and the behavior of aluminum. NOX emissions from combustion of double-base material are notably higher than from combustion of traditional fuels with similar nitrogen contents. Essentially all of this NOX is formed through fuel-bound NOX mechanisms. The data suggest that thermal decomposition of the EMDF leads to essentially quantitative formation of NOX from fuel nitrogen, unlike traditional fuels. Nevertheless, the NOX should be treatable by the same down-stream treatment techniques as are effective with other fuels, i.e., selective noncatalytic reduction by injecting, for example, ammonia. When blended with traditional fuels, NOX emissions from double-base materials will not be prohibitive.

NOX emissions from propellant binders are much lower than for double-base materials, but still are appreciable. The data suggest much greater contributions from thermal and prompt mechanisms, possible because of extremely high aluminum particle temperatures. These issues are also not prohibitive if the EMDF is blended in modest quantities with traditional fuels.

Management of the inorganic portions of some EMDFs may pose potential deposition and equipment problems. Aluminum particles attain high temperatures, well above their melting points, and remain at high temperatures for 1.5 s or more, which is long compared to residence times available in the furnace sections of most commercial boilers. Extreme temperatures of aluminum particles could pose some hazard to grates and kilns, where they are in potential intimate contact with surfaces. In our experiments, aluminum-containing EMDFs exposed to greater than 12% O2 melted though alumina fibers on a mat. Careful management of the fuel on a grate or in a kiln or combustion in suspension may prevent damage to systems at commercial scale. The large quantities of aluminum (60% of fuel mass) in many EMDFs could potentially overwhelm particle cleanup devices, even though the particles tend to form large and easily collected fly ash. These issues could be managed by limiting the fraction of EMDF in the blended boiler fuel.

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