Current Progress on the Use of Waste Energetic Materials as Fuel Supplements for Industrial Combustors

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ABSTRACT

An alternative disposal technology for waste energetic materials which has demonstrated potential for future applications at military installations is the reuse of these materials as a supplemental fuel for industrial combustors. The Department of Defense, over time, has accumulated a significant stockpile of waste energetic materials which requires disposal. The current disposal options, incineration, open burning and open detonation, are either cost prohibitive or under environmental scrutiny. An alternative disposal technology which shows promise is the reutilization of these energetic material;s as a supplemental fuel. Initial studies have indicated that it is feasible and economical to utilize the energy content from explosives and propellants to supplement fuel oil in industrial boilers. Significant progress has been made on the development on the process to use explosives as a supplemental fuel. Previous pilot scale tests and initial tests from a pilot scale demonstration at Hawthorne Army Ammunition Plant, Hawthorne, Nevada, have clearly demonstrated that explosives fuel oil mixtures can be safely fired into a standard industrial boiler. A state-of-the-art pilot scale system was designed and constructed for solvating and mixing explosives with fuel oil and firing the resultant mixture into a into a boiler to generate steam. Future tests are scheduled to increase the quantity of explosives in the fuel mixture and obtain additional process design information for full scale implementation. A feasibility study and a hazard analysis to determine the propagation potential for propellant/fuel oil slurries has recently been completed. The current progress and background with emphasis on the safety aspects on the use of explosives and propellants as a supplemental fuel are described.

INTRODUCTION

The Army, as the sole Department of Defense manager for explosives, is currently evaluating and developing safe,

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environmentally acceptable, alternative disposal and reuse technologies for it's stockpile of waste energetic materials. Waste energetic materials are propellants, explosives, and pyrotechnics and are commonly referred to as PEP. Unserviceable PEP materials are generated from the manufacture of PEP materials, assembly of munitions and demilitarization of obsolete conventional munitions. It is estimated that approximately 2.5 million pounds of scrap and off-specification energetic materials are generated each year[1]. In addition, there were an estimated 200,000 short tons of conventional munitions requiring demilitarization in 1990.

The disposal alternatives for these unserviceable PEP materials are open burning/open detonation (OB/OD) and incineration[1]. OB/OD is the preferred method of disposal, however it's use requires a Resource Conservation and Recovery Act (RCRA) Subpart X permit and due to environmental concerns, OB/OD is only allowed on a case by case basis. Incineration of energetic materials is uneconomical. To safely burn these materials, energetic materials are mixed with 75% water to form an energetic material/water slurry. The water is required to prevent detonation propagation during the handling and feed process. The addition of water increases the amount of fuel required to incinerate the energetic materials. Although OB/OD and incineration are acceptable disposal technologies, neither technology takes advantage of the energy content of these materials.

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) began investigating the feasibility of reusing the energy content from waste energetic materials to produce steam and/or electricity in 1984. Since explosives are a major waste energetic material in the U. S. Army's inventory, the USATHAMA began investigating the potential of using trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), and Composition B (40% TNT and 60% RDX) as a supplemental fuel.

BACKGROUND ON THE USE OF EXPLOSIVES

FEASIBILITY STUDY

In 1985, the Oak Ridge National Laboratory conducted a study to determine the feasibility of utilizing energetic materials as a supplemental fuel for industrial combustors [1]. This study examined the economics under different scenarios in which energetic materials might be economically used to generate steam and/or electricity in industrial combustors. The study also compared the costs of using energetic materials to the currently available disposal methods. The conclusion of this study determined that the cofiring of explosives could be economically competitive if existing oil-fired combustors at military production and demilitarization facilities were used without major combustor modifications.

PARTICLE SIZE REDUCTION

Since TNT and RDX are relatively insoluble in fuel oil, an explosives supplemented fuel oil would have to be burned as a slurry. Efficient burning of fuel oil requires atomization before combustion. Since standard oil burner designs use small holes to effect atomization, the energetic materials would have to be reduced to an acceptable size. Conventional techniques for energetic material size reduction, employing the grinding of the materials in water, results in a mean particle size to large for use with standard oil burners. A concept was proposed to reduce the particle sizes of TNT, RDX and Composition B by dissolution in a solvent such as acetone or toluene.

COMPATIBILITY, HANDLING CHARACTERISTICS, AND REACTIVITY

A second major area of investigation in the development of this technology was the evaluation of potential safety issues associated with the handling and burning of various mixtures of explosives, solvents, and fuel oil [2]. Testing was conducted to determine the chemical compatibility and stability, handling characteristics, and reactivity of the energetic-fuel mixtures. The chemical stability of explosives and fuel oil were determined by differential thermal analysis, vacuum thermal stability, and accelerating rate colorimetry. Results indicated that the fuel oil-energetic mixtures were chemically compatible. In addition, laboratory tests indicated that explosives/fuel oil mixtures could be handled safely.

The major areas investigated in handling energetic-fuel mixtures were the solubility of the energetic in the fuel, the viscosity of the energetic-fuel mixture, the energetic particle size distribution, and potential for nozzle plugging [2]. To achieve effective atomization in an oil burner the viscosity of the resultant energetic-fuel oil mixture should not exceed 30 centistokes. The results of the solubility and viscosity tests did not establish the upper boundary limits for the composition of the energetic-No. 2 fuel oil mixtures. The optimum compositions would have to be dictated by the propagation tests.

Bench-scale studies to determine the particle size limitations of the slurry using standard burner nozzle configurations indicated that no plugging problems should arise with the use of acetone or toluene for particle size reduction at the concentrations of concern. Although plating tests indicated a thin film of TNT was deposited on the surfaces of stainless steel when exposed to mixtures of TNT and fuel oil for at least 6 months, the surface buildup is easily removed by flushing with warm acetone.

Propagation tests were performed to establish the propagation of detonation characteristics of solvent solutions and fuel oil slurries of TNT and RDX [2]. These tests were run to determine the maximum allowable concentrations of explosives that can be safely transported in process piping. Both static and dynamic tests were performed. Static tests were conducted in a 2 inch horizontal pipe in which the explosives were allowed to settle out for 8 hours. Mixtures of TNT-toluene showed no propagation in both static and dynamic tests up to 65 wt.% TNT. Under dynamic tests, RDX concentrations up to 15 wt.% did not propagate a detonation. RDX/toluene mixtures, however, did propagate a detonation under static testing at >5.3 wt.% RDX. This was due to RDX particles settling and forming a trail on the bottom of the pipe. The limitation on the concentrations of explosives that can be used to supplement fuel oil is the quantity required for static propagation of detonation.

Although the limited solubility of RDX in toluene causes concern for the potential of burner nozzle plugging, toluene was selected as the solvent of choice for future pilot demonstrations. Toluene has a heating value and cost comparable to fuel oil. If acetone where used, for economic reasons nearly all of it would have to be recovered by evaporation before the mixture was fired into the combustor.

PROTOTYPE PILOT-SCALE DEMONSTRATION

In 1987, the first pilot scale demonstration on the cofiring of explosives/fuel oil mixture was conducted at Los Alamos National Laboratory using a 300 kW (10^6 BTU/hr) combustion chamber [3]. The combustor was operated using fuel oil supplemented with TNT, RDX and Composition B. The pilot scale system was designed upon the fuel blending and feed requirements and safety issues described above. Although the tests were discontinued because of equipment failure, a sufficient amount of data were obtained which clearly showed that explosives can be safely cofired with fuel oil. The data indicated that explosives could be cofired using off-the shelf equipment, the process would meet present and anticipated environmental requirements and several design and operational changes were necessary.

ECONOMIC ANALYSIS OF USING EXPLOSIVES

Myler described the economics of cofiring TNT and Composition B by comparing it to an industrial boiler using No. 2 fuel oil [6]. A supplemented fuel containing 55% No. 2 fuel oil, 15% TNT, and 30% toluene was compared using a 20 MBtu/hr boiler. This is the standard size package boiler used at military installations. Operating at 80% efficiency, it was estimated that 480 short tons/year of waste TNT could be disposed of using this technology. In addition, the analysis indicated that as fuel costs rise, the use of waste explosives as a fuel supplement would be profitable. The break even point was a cost for No. 2 fuel oil of $0.83 per gallon with a constant toluene cost of $0.93 per gallon. Since this study, the fuel oil prices have risen above this point which implies there would now be a net profit for burning the supplemented fuel at the ratios previously described.

PILOT-SCALE FIELD DEMONSTRATION USING EXPLOSIVES

EQUIPMENT DESIGN AND PROCESS

In 1989, a state of-the-art pilot scale system was designed and constructed for mixing explosives with fuel oil and firing the resulting mixture into a standard industrial boiler to generate steam [4,5]. The test equipment was designed to meet strict safety standards involved in the handling of explosives and volatile solvents. The major process equipment items in this pilot scale system are the explosives dissolving system, the fuel/explosives blending tank, the boiler and steam vent system and boiler management system. A prototype explosives dissolving and blending system was designed to dissolve the explosives in solvents, mix the solvent-explosives mixture with fuel oil, and feed the resultant mixture to the boiler system. The dissolving tank and blending tank were constructed of stainless steel. There are two dissolving tanks with air actuated mechanical mixers. These tanks were indirectly heated using steam from the boiler. The blending tank was not steam heated and used an air diaphragm pump to mix the explosives solution with the fuel oil and feed the resultant mixture to the boiler.

The boiler selected for the pilot scale system was a standard Cleaver Brooks Model M4000, 2 million Btu/hr, water tube-type boiler. This size boiler is one tenth the scale of the majority of boilers used at Army facilities. This standard boiler was modified to meet the required electrical specifications and the burner assembly modified with three burner assemblies for the propane pilot, the fuel oil, and the explosives-fuel oil solution. The burners were sonic atomizer type nozzles. The boiler management system consisted of a boiler and a feed system control panel located in an underground control room. The boiler control panel provided instrumentation for monitoring and recording data from the boiler and boiler feed water system. Flame interlocks and boiler management were provided by a Honeywell Model BC 7000 microcomputer burner control system. The explosives dissolving and blending system control panel provided instrumentation for monitoring and recording data from the explosives mixing system. Interlocking and sequencing of the explosives solutions were provided by a Allen Bradley programmable logic controller (PLC). A process flow diagram of the equipment is shown in figure 1.

Once the boiler is fired with fuel oil and is brought up to sufficient operating temperatures, a specified quantity of explosives is dissolved into a quantity of solvent (toluene) in one of the explosives dissolving tanks. The explosives are dissolved by mixing and indirect heating with steam from the boiler (100°F). The explosives/solvent solution is mixed with the fuel oil in the explosives blending tank and continuously mixed by the air diaphragm pump. The fuel oil/solvent/explosives solution is then fed to the boiler to produce steam. A sufficient quantity of excess air is maintained to ensure complete combustion. After operations, acetone is flushed through the system to decontaminate the system.

FIELD DEMONSTRATION TEST

The field demonstration test was initiated at Hawthorne Army Ammunition Plant, Hawthorne, NV, in October 1990 using the pilot scale system previously described[4]. Weston, Inc. was the contractor for this demonstration. The objectives of the pilot scale test were to determine the destruction efficiency of the system, to characterize the gaseous effluent, to identify operational and safety problems, and to evaluate the potential for future use of the technology on full scale operations. Prior to the operation of the pilot system a Hazard Analyses was conducted by Hercules Incorporated, Allegany Ballistics Laboratory. In addition, a Safety Plan and a Site Plan/Safety Submission were prepared, reviewed, and approved by all safety organizations in the chain of command including the Department of Defense Explosives Safety Board.

A total of eighteen tests were scheduled. There were three test sequences based on the type of fuel processed: Test Sequence I - No. 2 fuel oil only, Test Sequence II - No. 2 fuel oil/solvent/TNT, and Test Sequence III - No. 2 fuel oil/solvent/Composition B. A matrix of explosives concentrations and excess air percentages were scheduled. Figure 2 contains a summary of the planned tests and sequences.

TEST RESULTS AND CONCLUSION

Due to the expiration of Weston's research and development contract with USATHAMA, only five of the scheduled tests were conducted. Since there was a time constraint, the tests were conducted out of order. Three tests were completed using fuel oil only (T1, T2 and T3). These were used to characterize the boiler combustion characteristics, particularly nitrous oxide emissions at excess air levels ranging from 20% to 30%. Only the test using the 1% TNT in toluene (T5) with 30% excess air was completed satisfactorily. The pilot scale system was decontaminated with acetone, and the remaining tests canceled due to the expiration of Weston's contract.

Although the tests were not completed as scheduled, the technology once again demonstrated the potential to be an effective method to recover energy from waste explosives. Dilute solutions of TNT (1%) were safely and effectively used to supplement No. 2 fuel oil in an industrial boiler. A destruction and removal efficiency of 99.99% was achieved while cofiring this dilute solution of TNT. The nitrous oxide emissions were characterized for the tests completed and, as expected, the nitrous oxide emissions increased significantly when cofiring the explosives supplemented fuel. Several design modifications were identified which will be implemented before continuation of the tests.

CURRENT EXPLOSIVES PROGRAM

After significant delays, the previously scheduled tests are scheduled to resume at Hawthorne Army Ammunition Plant in 1993. The original test matrix will be repeated with the new system modifications. Although the propagation testing established the upper limits of explosives content that could be safely utilized in this technology, the ability to meet the air quality standards will establish the maximum explosives concentration limits. In addition, since this process will likely fall under RCRA, the limits may be established by the ability to achieve a 99.99% destruction rate efficiency and an average carbon monoxide emission limit of 100 ppm over a 60 minute period (corrected to 7% oxygen). It is also very likely that the nitrous oxide emissions will be a key parameter in obtaining environmental permits for this technology. Once the emissions from scheduled tests have been quantified, several engineering designs will be evaluated to optimize the process and reduce the emission within regulatory limits.

CURRENT PROGRESS ON THE USE OF PROPELLANTS

TECHNICAL AND ECONOMIC ANALYSIS

The Tennessee Valley Authority (TVA) - National Fertilizer and Environmental Research Center began investigating the feasibility of using propellants as a supplemental fuel for industrial combustors in 1990 [7]. A series of laboratory tests were conducted to evaluate the physical and chemical characteristics, as well as the chemical compatibility, of nitrocellulose-solvent-fuel oil mixtures. Unfortunately, these test indicated that solvation and mixing with fuel oil was not technically feasible or cost-effective due to the low solubility of nitrocellulose. However, an economic analysis did indicate potential cost effectiveness of using propellant-fuel oil slurries as supplemental fuels.

A technical and economical study was completed by TVA on the use of propellant-fuel oil slurries as a supplemental fuel in September of 1991[8]. The propellants studied were nitrocellulose, nitroguanidine, and AA2 double-base propellant. A series of tests were conducted to determine the physical and chemical characteristics, as well as the chemical compatibility, of propellant No. 2 fuel slurries. The propellant-fuel oil mixtures were determined to be compatible and stable. In addition, it was found that wet-grinding of AA2 double base propellant with No. 2 fuel oil using an Ultra-Turrax grinder was sufficient to reduce the particle size to acceptable levels. This study concluded that a 10 percent by weight nitrocellulose-, nitroguanidine-, or AA2 propellant No. 2 fuel oil slurries as supplemental fuel was a cost-effective disposal option. The 10 percent by weight concentration of propellant in the slurry was based on the viscosity that could be handled by a conventional, unmodified burner. Larger quantities could be disposed of, if burners could be retrofitted to handle fuels with higher viscosities.

PROPAGATION TESTING

Zero gap propagation of detonation tests were conducted to determine the sensitivity of propellant-No. 2 fuel oil slurries to detonation of a shock wave[9]. Two operational modes were evaluated: the dynamic or pumping mode, and the static or settled slurry mode. Supplemented fuels containing 10 percent by weight nitrocellulose, 15 percent by weight nitroguanidine, and 20 percent by weight AA2 double base propellants slurried in No. 2 fuel oil did not propagate a detonation in either operational modes.

CURRENT PROGRAM

The results of the laboratory and bench-scale studies have indicated the technical and economical feasibility of utilizing propellants as a supplemental fuel. The U.S. Army Toxic and Hazardous Materials Agency is currently negotiating a Memorandum of Agreement with the Naval Surface Warfare Center - Indian Head, Maryland, to establish a joint Service program to continuing the development efforts of the propellant supplemental fuel program. After completion of the tests using explosives at Hawthorne Army Ammunition Plant, the pilot scale system will be moved to Indian Head, Maryland. A pilot-scale demonstration on the use of propellant-fuel oil slurries is planned for the future.

CONCLUSION

Although additional research and development is needed before full-scale application of this technology, significant advancements have been made in the development of this technology. The future implementation of this technology could prove to be a cost-effective disposal alternative to incineration and OB/OD which will not only benefit the DOD but commercial industry as well.

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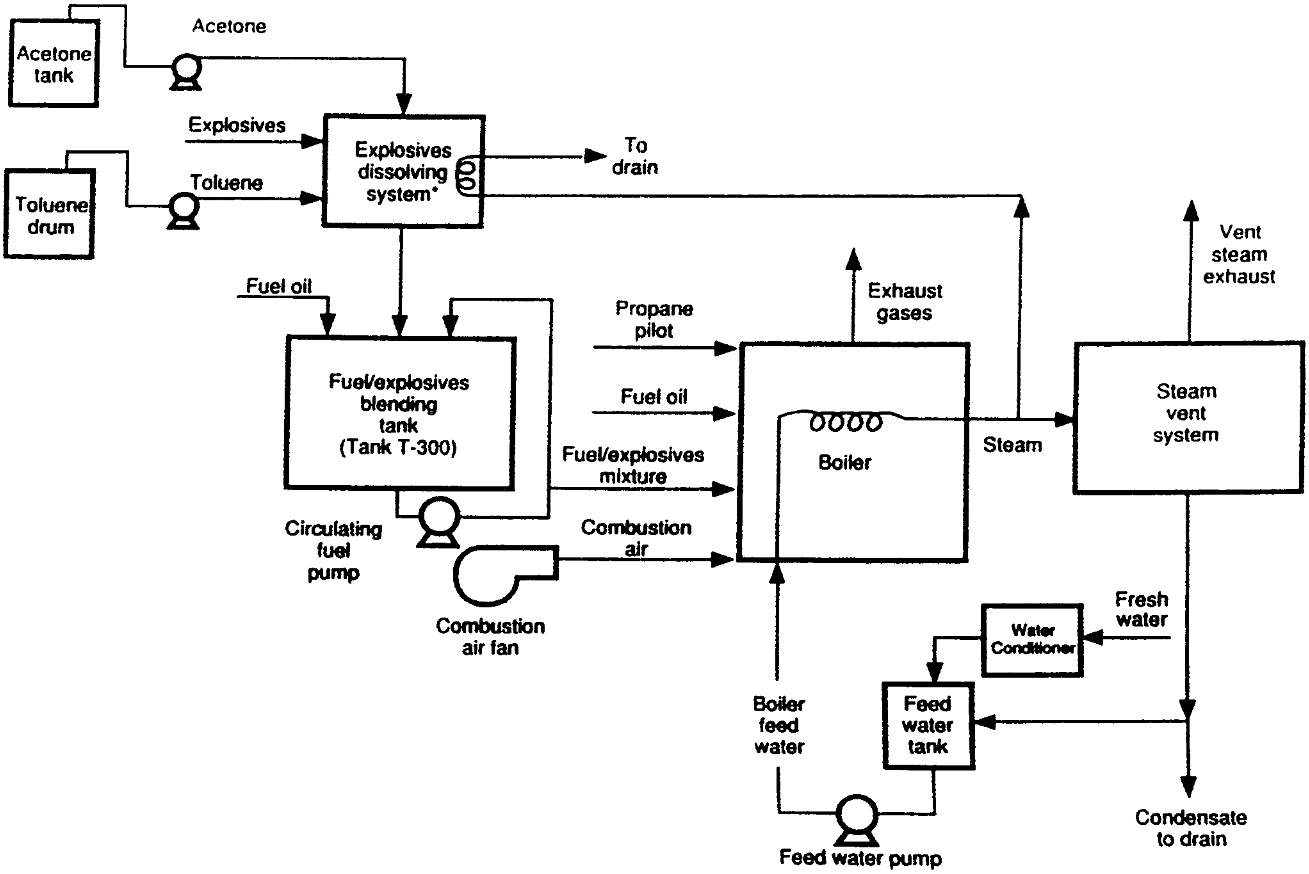

Figure 1
Process Flow Schematic

Test Sequence I

- Fuel oil feed
- Various excess air concentrations (20%, 25%, 30%)

% excess air	
20	T-1
25	T-2
30	T-3

Test Sequence II

- Fuel oil/solvent/TNT feed
- Various excess air concentrations

% excess air	Weight % explosives in feed		
	1	10	15
20	T-10	T-7	T-9
25	T-12	(T-18)* T-11	T-8
30	T-5	T-6	T-4

Test Sequence III

- Fuel oil/solvent/Comp B feed
- Various excess air concentrations

% excess air	Weight % explosives in feed		
	1	4	8
20	T-16		T-14
25		T-17	
30	T-13		T-15

*T-18 was a repeatability test.

Figure 2
Planned Test Sequences