Use of waste energetic materials as a fuel supplement in utility boilers

Craig A. Myler

U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD 21010-5401 (USA)

William M. Bradshaw

Oak Ridge National Laboratory*, Oak Ridge, TN 37831 (USA)

and

Michael G. Cosmos

Weston Services, Inc., West Chester, PA 19380 (USA)

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Abstract

Waste energetic material produced during the manufacture of explosives has been considered a by-product waste which must be disposed of. Methods such as open burning or open detonation pose potential environmental risks while disposal in specially designed hazardous waste incinerators is costly. No current method capitalizes on these materials' inherent energy capacity. Efforts to utilize these wastes as supplements to fuel oil are under way. Laboratory and bench scale operations verify the principle while economic analysis shows a positive advantage using this approach. Pilot scale testing is in progress to develop fuel mixing/feeding procedures and to determine fuel mixture energy parameters.

Introduction

Production and stockpiling of explosives by the U.S. Army results in the generation of waste energetic materials. Typically, these materials contain nitrated aromatic compounds which are classified as hazardous due to their inherent reactivity. Environmentally safe methods are used to dispose of these materials as hazardous wastes; however, they do not take advantage of the energy content of these materials. A program initiated by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) in conjunction with Oak Ridge National Laboratory (ORNL) and Roy F. Weston, Inc. is investigating

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the use of these waste materials as a supplement to fuel oil for use in standard industrial-type boilers. Using the energy stored in these wastes reduces fuel consumption while eliminating potential hazardous waste. Each of these benefits is a national priority item. The development of this technology is therefore highly desirable.

Nature of the waste

To effectively treat the subject, a description of the nature of the wastes as well as their origin is in order. Energetics are separated into three classes: (1) propellants, (2) explosives, and (3) pyrotechnics. Propellants and pyrotechnics will not be included in this report. This does not preclude their use as fuel supplements and work has been initiated to investigate the use of propellants as fuel supplements, either as admixtures to fuel oils or as supplements to coal.

The two primary explosive wastes of concern are trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX). These are the most prevalent explosives in use today and constitute the greatest inventory of waste. The structures of these compounds along with pertinent physical data are given in Figs. 1 and 2. Of particular note is the substantial amount of available nitrogen. This will be discussed in terms of expected combustion products later in this report. Often TNT and RDX are combined (normally with a small amount of paraffin) to form a composite explosive. The most common is Composition B or simply, Comp B, which is a 40% TNT to 60% RDX mixture.

As class A explosives, both TNT and RDX constitute a reactivity hazard. Handling, storage and use require special care and attention to insure the safety
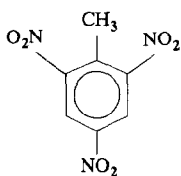

Fig. 1. Structure and physical properties of trinitrotoluene (TNT) [2].

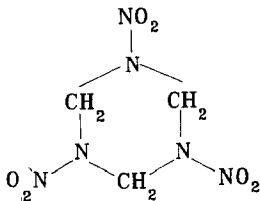| Melting point	80 to 81°C
Color	Yellow, crystalline
Boiling point	345°C
Density	1.654 g/cm^3
Viscosity	0.139 poise (13.9 mPa·s) at 85°C
Specific heat	251.8 J/mol·K at 27°C
Heat of combustion	809.18 to 817.2 kcal/mol
Solubility at 0°C	57 g/100 g acetone
	28 g/100 g toluene
Solubility at 50°C	346 g/100 g acetone
	208 g/100 g toluene

Fig. 2. Structure and physical properties of cyclotrimethylenetrinitramine (RDX) [3].

Melting point	202 to 203°C
Color	White, crystalline
Density	1.806 g/cm^3
Specific heat	277 J/mol·K at 20°C
Heat of combustion	501.8 to 507.3 kcal/mol
Solubility at 0°C	4.2 g/100 g acetone
	0.016 g/100 g toluene
Solubility at 50°C	12.8 g/100 g acetone
	0.087 g/100 g toluene

of personnel. In addition to its reactivity, TNT also constitutes a toxicity hazard. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a time weighted average (TWA) maximum concentration of 0.5 mg/m^3 and indicates a dermal hazard with TNT [1]. The risk associated with this toxicity is generally small, since TNT is a solid under standard conditions which has low solubility in water. Even so, this toxicity cannot be ignored in any program utilizing TNT. Necessary precautions include safe explosives handling techniques, precaution against skin contact, and insurance against airborne contamination. Safe explosives handling including prevention against skin contact is commonly practiced and will not be discussed further.

The heating value of RDX is approximately 9 kJ/g while for TNT it is approximately 15 kJ/g. Each of these compounds burns easily and completely. The largest drawback to utilization as fuel supplements (outside of their reactivity) is the production of toxic NO_x. Combustion of these explosives produces some quantity of NO_x above that which would be produced from the combustion of standard fuels. This NO_x production was found to be approximately 0.54 g/MJ of fuel [4]. Current test objectives include the characterization of these emissions and determination of means to curtail or treat the production of NO_x.

Sources of the waste

Along with the preceding discussion on the chemical nature of the waste, a brief description of the source of the waste and its physical state is in order. Two sources contribute to the inventory of waste explosives. The first of these is the normal production process. The second source is that inventory which

becomes either obsolete due to its packaging or unserviceable due to storage, damage, etc.

As in the production of most items, especially in batch-produced chemicals, off-specification materials are sometimes produced. Due to the military nature of explosives, strict production specifications are enforced. Batches of explosives sometimes fail to meet specifications, which leads to their classification as wastes. Lackey [5] provides an estimate of current energetic waste generation of 1.13×10^6 kg/y. This estimate grows to 4.60×10^6 kg/y during full scale production. It should be noted that no TNT is currently produced. Additionally, loading of munitions with explosives results in significant waste generation through equipment wash down procedures.

The second source of waste explosives is unserviceable stockpiles. If a weapon is no longer a part of the Army inventory, the munitions it uses may be classified as unserviceable or obsolete. Also, quality control of stockpiled munitions may determine that a particular munition is unable to meet requirements for military service and it will be classified as unserviceable. This may be due to the breakdown of the explosive itself, degradation of other chemical portions of the munition such as a propellant charge, or to a deterioration of the munition body (for example a corrosion of the casing). Table 1 provides an estimate of the amount of unserviceable explosives in the current Army inventory.

Finally, current disposal practices will be discussed. Two methods are generally used, not including continued storage which by its nature is expensive and non-productive. The first is destruction by open detonation of the explosives. This practice is simple, relatively safe and expedient. It has recently come under environmental scrutiny and testing is currently in progress to determine the impact of this disposal method on the environment. Open detonation does not capitalize on the heating value of the explosives.

The second current method of disposal is by incinerating the waste explosives. Typically, the explosive is mixed to form a water–explosive slurry and fed to a rotary kiln. A fuel such as propane or fuel oil is used to maintain the kiln temperature at approximately 1200°C. This process requires approximately 1.67 kg of fuel oil per kg of explosive destroyed. Although this process

TABLE 1

Estimate of unserviceable explosives ($\times 10^6$ kg) contained in U.S. Army stockpile (1985, [6])

Source	Explosive	
	Comp B	TNT
Munitions	2.535	1.496
Reclaimed material	2.315	–
Total	4.850	1.496

can be made environmentally acceptable, it is expensive in terms of capital cost and energy consumption.

Neither of the above disposal practices takes advantage of the energy contained in the explosives. With limited government resources being a constant concern, a less costly alternative approach is desirable. In the case of mobilization for national defense, limited fuel reserves makes utilization of this energy source even more important.

Safety

Safety is of paramount importance in using explosives as fuel supplements. The very nature of explosives requires special handling during their intended use and even stricter controls during combustion in an industrial boiler. Three separate areas of concern will be addressed. First, the rheology of explosives–fuel oil mixtures will be discussed. Second, physical properties with impact on compatibility of the explosives with fuel oils will be described. Finally, the likelihood of detonations occurring is addressed. These three safety related areas are fully described by Lackey [7].

Rheology of explosives–fuel oil mixtures

Due to the physical state of the waste explosives (irregularly sized solid pieces) and the relatively low solubility of TNT and RDX in fuel oils, a solvent is used to bring the TNT and RDX into solution. At some concentrations the RDX and TNT form slurries, especially upon removal of the solvent. Also, mixtures of toluene, TNT and fuel oil were shown to produce multiphase liquid mixtures which are undesirable for feed to a boiler. An optimum composition for the supplemented fuel must be determined and has an upper boundary dictated by detonation potential which will be described later.

Proper combustion of fuel oils is dependent on the burner systems' parameter to atomize the fuel. Viscosity is a key design parameter in selection of an atomizing nozzle and burner. Viscosity data for TNT supplemented fuel oils is given in Table 2. As shown, the viscosity of a No. 2 fuel oil supplemented with TNT does not show a significant increase in viscosity due to the addition of the explosive.

TABLE 2

Viscosity (in centistokes or mm^2/s) of TNT supplemented fuel oils at various concentrations [8]

Fuel oil	TNT (g/100 ml fuel oil)				
	0	10	15	20	30
No. 2 at 38°C	3.7	4.2	4.4	4.7	–
No. 5 at 60°C	37.0	56.0	–	75.0	106.0

Explosives-fuel oil compatibility

Consideration was given to the chemical compatibility of TNT and RDX with fuel oil [7]. Differential thermal analysis, vacuum thermal stability and accelerating rate calorimetry all showed that neither TNT nor RDX undergo chemical reaction in the presence of fuel oil and/or solvents but act simply as solids in solution. A test to determine if TNT would plate out in solution over time was conducted as well. Plating was observed during this 6 month long test; however, the plating was only a thin layer which presented no hazard when removed with warm acetone. Plating of TNT in current tests will be prevented by frequent feed system washing with warm acetone.

Detonation testing

Finally, testing of the detonation characteristics of supplemented fuel oil was conducted [7]. Both static and dynamic tests were performed. Static tests were conducted in a horizontal 0.0504 m (2 inch, sched 40, 304 SS) pipe in which the explosive-supplemented fuel was allowed to settle for a duration of 4 to 8 hours. Dynamic tests were conducted in a vertical pipe of the same diameter in which the mixture was agitated and then immediately tested for detonation potential. Single phase TNT–acetone–No. 2 fuel oil mixtures showed no propagation of detonation characteristics in static tests at TNT concentrations up to 78 wt.% (percent by weight). Mixtures of TNT–toluene showed no propagation in both static and dynamic tests at up to 65 wt.% TNT. On the other hand, RDX did result in propagation of detonation for static testing at 5.3 wt.%. This was due to RDX particles settling and forming a trail on the bottom of the pipe. For dynamic testing, RDX concentrations up to 15 wt.% did not exhibit propagation of detonation. Supplemented fuels containing less than the concentration required to support propagation of detonation in the static mode will be used in testing.

Pilot testing using a prototype combustor

In 1987 a pilot scale (300 kW) combustor was operated using fuel oil supplemented with TNT, RDX and Comp B [9]. Testing was conducted at the Los Alamos National Laboratory. Mechanical problems with the equipment precluded completion of this test program but not before sufficient data were acquired to show that the use of explosives as fuel supplements was possible. The problems encountered consisted of the failure of the insulation used in the reducing section of the prototype combustor and the failure of the burner tip caused by RDX accumulation and subsequent burning. Enough data were taken to warrant a continuation of the pilot scale testing with careful attention given to selection of a combustion chamber and the feed system used to introduce the explosive supplemented fuel oil. A diagram of the prototype combustor is shown in Fig. 3.
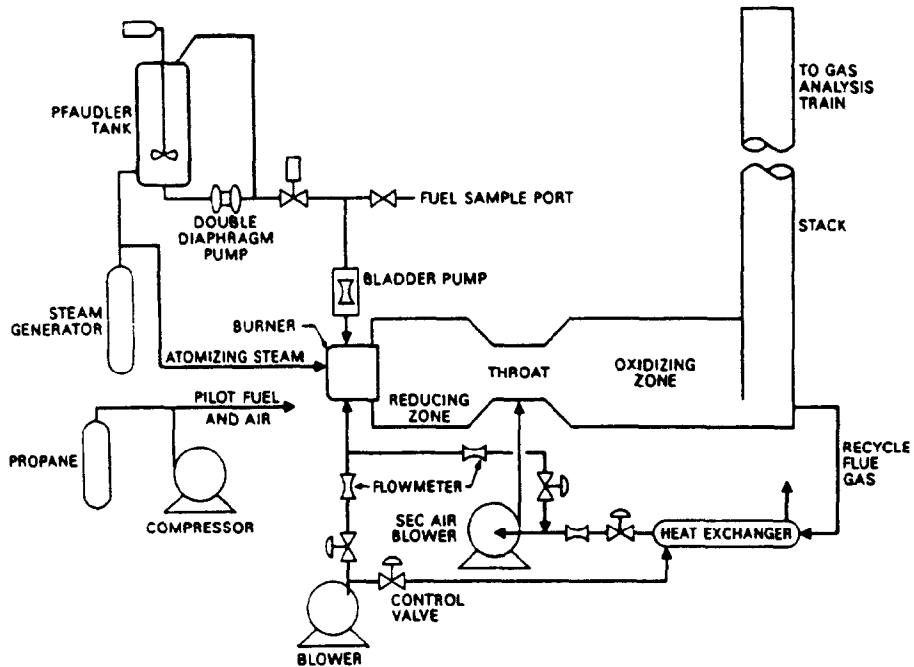
Fig. 3. Prototype combustor used in initial pilot scale studies [9].

In addition to showing the feasibility of utilizing explosive supplemented fuels, stack emissions data were obtained from the prototype combustor. These data were collected and reported by the Army Environmental Hygiene Agency [4]. As only four data runs were performed in which stack sampling was conducted, only generalized conclusions could be reached. The first conclusion is that destruction and removal efficiencies (DRE) of 99.999% were obtained for TNT combustion. Carbon monoxide and particulate emissions were described as controllable. Finally, and perhaps most important, increased NO_x concentrations were found to be caused by the addition of the explosives to the fuel oil. With the limited number of data points obtained and the poor condition of the combustor it is premature to formalize estimates of NO_x production for design of control equipment. It should be noted that the NO_x emission rate was reported for total NO_x as NO_2. For the two data points obtained during supplemented fuel burns, the total NO_x emission rate was between 0.50 and 0.56 g/MJ. Methods to curtail this production rate as well as obtain definitive data to support design of abatement systems are key factors in current test plans.

Current program

Using the foregoing information, USATHAMA's current program was developed to provide the data needed to specify requirements for a complete sup-

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plemental fuel system utilizing TNT or Composition B. Testing has begun in June 1990. Three major items required to obtain a working pilot system are: (1) a boiler system which would approximate the anticipated full scale boilers that the supplemented fuels would be used in, (2) a system to safely mix and feed the explosives, solvent and fuel oil, and (3) a data acquisition plan to obtain the necessary design information for both emission control design, the operating parameters for the burner and preliminary data needed for regulatory approval. A block diagram of the test system is shown in Fig. 4.

The boiler is the central piece of equipment in the utilization of explosives-supplemented fuels. The majority of currently installed oil-burning Army steam boilers are of a water tube design. Various burners and nozzles are used. For the current tests, air atomization was selected to reduce the potential for flashing of the toluene in the supplemented fuel mixture. The boiler selected is designed for 47 boiler horse power and utilizes fuel at an input rate equivalent to 498 kW. A scale factor of ten would include the majority of process steam generation boilers in use today. Larger systems are used; however, more complex burner designs and fuel feed systems would likely require additional testing prior to use of supplemented fuels in these systems. This testing would
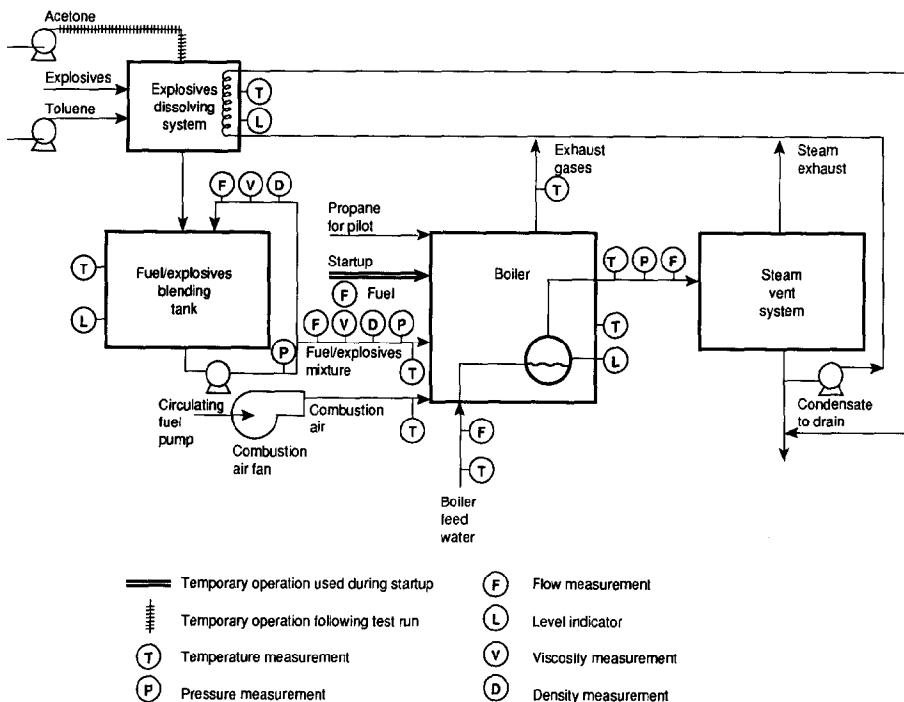

Fig. 4. Block diagram of supplemental fuel pilot scale system.

likely include surrogate fuel mixtures synthesizing the viscosity and heating value of the supplemental fuel.

The second required piece of equipment for this test program is the mixing/feed system. This unit is currently in the design stage and will include provision for dissolving the explosives in a separate solvent tank, followed by remove addition of this solution to a fixed quantity of fuel oil. The system will mechanically agitate the fuel mixture as well as recirculate the mixture through the piping system. Once a test is completed (by exhaustion of the supplemented fuel mixture), the system will be flushed with acetone by remote control. The mixing/feed system would constitute the primary capital cost for implementation of a system to utilize waste explosives. Care in terms of scalability by utilizing standard equipment in the pilot scale design will assist in the scale up of this unit to a full production system.

Finally, the data acquisition plan was designed to obtain the necessary information for implementation of this technology. This includes flow properties of the selected feed mixtures, efficiency of explosive destruction within the system, heat balances over the system and measurement/characterization of emissions from the system. Eighteen total tests will be conducted. The sample matrices for supplemented fuel experiments are shown in Fig. 5 and the expected test sequence is shown in Fig. 6. In addition to the 14 tests shown in Fig. 5, three tests will be performed using No.2 fuel oil without the addition of explosives and one test will be performed as a duplicate test using supplemented fuel oil.

Fig. 5. Test matrices for TNT and Composition B supplemented fuels pilot scale testing.

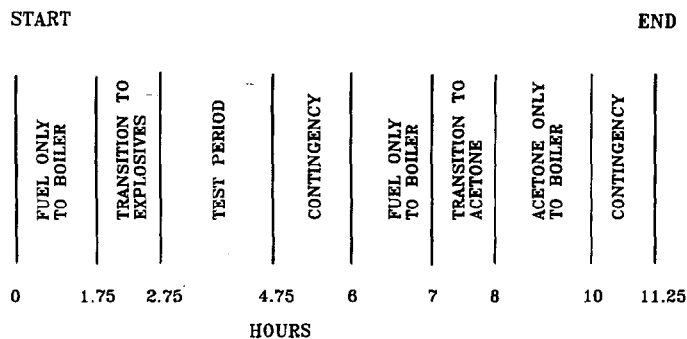START   END

Fig. 6. Expected test sequence for explosive supplemented fuel pilot scale testing.

Conclusion

The use of waste explosives as supplements to fuel used in steam boilers appears to be a viable means of using for fuel what would otherwise be a difficult to dispose of waste product. Previous work has shown the feasibility of using waste explosives as fuel supplements in terms of safety, hazardous waste elimination and cost. Current project plans are aimed at providing the necessary information to make this technology available for implementation at Army installations. By eliminating a hazardous waste through utilization of its energy potential, effective use is made of what is otherwise a costly environmental problem.

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