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Feasibility of using nitrocellulose–solvent–No. 2 fuel oil solutions as fuel supplements for industrial combustors

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Abstract

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is currently conducting a program with the Tennessee Valley Authority (TVA) to determine the feasibility of utilizing propellants as supplemental fuels for the U.S. Army's industrial combustors. Disposing of obsolete and waste propellants in this manner could be both cost-effective and environmentally sound, and as an added benefit would utilize the energy value of these materials. Tests were conducted to evaluate the physical and chemical characteristics, as well as the chemical compatability, of nitrocellulose (NC)–solvent–No. 2 fuel oil solutions. Acetone, ethyl acetate, and butyl acetate were tested as solvents for NC. The results from these tests, coupled with an economic analysis, indicated that solvation of NC with the best solvent tested, acetone, and mixing with No. 2 fuel oil was not technically feasible or cost effective due to the low solubility of the NC. However, the economic analysis did indicate potential cost effectiveness using propellant–No. 2 fuel oil slurries as supplemental fuels.

Introduction

The Department of Defense (DOD) currently has a large inventory of waste propellants which are contained in conventional munitions that are obsolete or no longer serviceable. Additional quantities of waste propellants are generated during the normal process of manufacturing these materials. Currently available options for disposing of obsolete or out-of-specification propellants

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are open-burning/open-detonation (OB/OD) or incineration [1, 2]. However, these options are being severely restricted by federal and state environmental regulations. For example, OB/OD of energetic wastes requires a Subpart X permit under the Resource Conservation and Recovery Act. Subpart X operations remain under interim status until the final regulations have been issued. At that time, whether or not OB/OD operations will be allowed to continue in their current form is unknown [3]. Incineration is costly and does not capitalize on the recovery of energy from these energetic wastes. A technically feasible and cost-effective option to OB/OD or incineration is needed to dispose of waste propellants.

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) is currently investigating procedures for utilizing waste trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX) as supplemental additives to fuel oil for the recovery of energy from these compounds [4]. The method used to introduce TNT and RDX as fuel additives involves solvation and mixing with No. 2 fuel oil. A pilot scale demonstration test to determine the feasibility of using these explosives as supplemental fuel for use in standard industrial-type combustors is in progress [5]. As a logical extension of this program, USATHAMA is now sponsoring a project with the Tennessee Valley Authority's National Fertilizer and Environmental Research Center to investigate the use of waste nitrocellulose (NC)-based propellants as a supplemental fuel for standard industrial combustors [6, 7].

Nature of waste propellants

Propellants that require disposal by the DOD primarily consist of single-, double-, and triple-base propellants. For a single-base propellant, 85–95 percent of the composition consists of NC; for a double-base propellant, the fraction of NC decreases to 55–78 percent, while for a triple-base propellant, only about 20–28 percent of the composition consists of NC. Since NC constitutes a large fraction of the waste propellant inventory, a feasibility study was initiated to determine if NC could be solvated and mixed with No. 2 fuel oil to provide a supplemental fuel for industrial combustors.

Military-grade NC is prepared by nitrating cotton linters with a mixed acid [8]. The resulting NC is a high molecular weight (10^5–10^6 g/mol) polymer chain composed of anhydroglucose units, each containing up to three nitrate groups. The nitrogen content determines the chemical and physical properties of any particular NC. NC containing from 12.9 to 13.5% nitrogen is known by the traditional name of "guncotton". Three other classes of NC are also used in the preparation of military propellants: pyrocellulose (12.6% nitrogen); blended (13.15–13.25% nitrogen); and pyroxylin (12.0–12.2% nitrogen). Blended NC (Grade C, Type I, 13.15% nitrogen) was purchased from Hercules, Inc. and used in the tests described in the following sections.

Characteristics of NC–solvent–No. 2 fuel oil solutions

Solubility of NC

There is one general rule to consider when compiling a list of candidate solvents for NC — no substance is a solvent unless its molecule contains a polar group [9]. Acetone, which contains a polar carbonyl oxygen (C=O) group, has been shown to be the most effective solvent for NC with various nitrogen contents [10–12]. Ethyl acetate and butyl acetate were also selected for use in the solubility tests based on a review of the scientific literature [12–16].

Each solubility test was conducted at 25 °C. The maximum concentration of NC in each solvent was limited by the ability of the solubility apparatus [17] to adequately stir the NC-solvent solution. For example, the maximum concentration of NC in acetone was 7.5 percent by weight. Above this concentration, the NC–acetone solution became a viscous gel and the experiment had to be terminated. Similarly, for ethyl acetate and butyl acetate, the maximum concentrations were 4.8% and 4.4%, respectively. NC was insoluble (<0.010 g/ml) in No. 2 fuel oil at this temperature.

Dilution ratios

The dilution ratio method (American Society for Testing and Materials (ASTM) D 1720-88), which involves the determination of the volume of diluent liquid required to just cause precipitation of a cellulosic material from solution, is often used as a means of assessing the solvent power of solvents for cellulose derivatives. This method also yields important technical information regarding the ability of solutions to tolerate additions of diluent liquids. The dilution ratio is defined as the total volume of diluent added to a solution divided by the total volume of solvent present.

The results from the dilution ratio tests with each solvent are summarized in Table 1. No. 2 fuel oil was used as the diluent, and the initial volume of solvent in each test was 50 mL. The maximum concentration of NC in each solvent was dictated by the fact that the NC–solvent solution had to be swirled by hand in order to carry out the dilution ratio test according to ASTM D 1720-88 standard procedure. Guideline maximum concentrations of NC in each solvent were previously established in the solubility tests.

NC–butyl acetate solutions tolerated the greatest additions of No. 2 fuel oil before precipitation of the NC occurred. However, the maximum concentration of NC in the butyl acetate to adequately perform the dilution ratio test was only 4.1%. A higher maximum concentration of NC in ethyl acetate (5.3%) could be attained than was the case for butyl acetate. However, the dilution ratios for the NC–ethyl acetate solutions were lower than for the NC–butyl acetate solutions. The highest concentration of NC (8.3%) could be added to acetone before it became impossible to swirl the solution in the flask. However, NC–acetone solutions were the least able to tolerate additions of the No. 2 fuel oil diluent before precipitation occurred.

TABLE 1

Summary of results from dilution ratio experiments for NC–solvent solutions

Solvent	NC Initial (wt. %)	Total solvent (ml)	Total diluent (ml)	Dilution ratio
Acetone	1.4	52.0	27.0	0.519
	3.7	51.0	24.0	0.471
	6.0	51.0	22.6	0.443
	8.3	52.0	21.5	0.414
Ethyl acetate	1.2	53.0	71.0	1.340
	3.3	52.0	51.2	0.985
	5.3	53.0	44.0	0.830
Butyl acetate	1.4	53.0	95.0	1.792
	2.8	52.0	85.0	1.635
	4.1	53.0	62.0	1.170

The data from the dilutions ratio tests established the amount of No. 2 fuel oil that could be added to an NC–solvent mixture so that the NC would remain in solution. These results were then used to prepare NC–solvent–No. 2 fuel oil solutions for subsequent viscosity, heat of combustion, and chemical compatibility testing. The results from these tests will now be discussed.

Viscosities

To obtain atomization in an oil burner, it is generally accepted that the kinematic viscosity of the fuel should not exceed a range of 20 to 30 centistokes (mm^2/s) at the burner tip [4]. The viscosities of the NC–acetone–No. 2 fuel oil solutions, measured with a falling ball viscometer (ASTM D 1343-86) at 20 °C and 50 °C, increase rapidly when the NC concentration is increased from 0.7 to 4.1% (Fig. 1). At an NC concentration of approximately 1.5% in a 66.5% acetone–32.1% No. 2 fuel oil solution, the viscosity of this solution at 20 °C will exceed the 30 centistoke upper limit to obtain atomization in a conventional oil burner. Similarly, at an NC concentration of approximately 1.8% in the same solution composition, the viscosity at 50 °C will exceed the 30 centistokes upper limit.

For ethyl acetate–No. 2 fuel oil solutions at 20 °C and 50 °C, the maximum concentrations of NC which could be tolerated before exceeding the 30 centistokes limit were 0.9 and 1.5%, respectively. For butyl acetate–No. 2 fuel oil solutions at 20 °C and 50 °C, the maximum concentrations of NC were 1.1 and 1.2%, respectively.

Heats of combustion

The heat of combustion data obtained from the blended NC, solvents, No. 2 fuel oil, and NC–solvent–No. 2 fuel oil solutions are given in Table 2. The

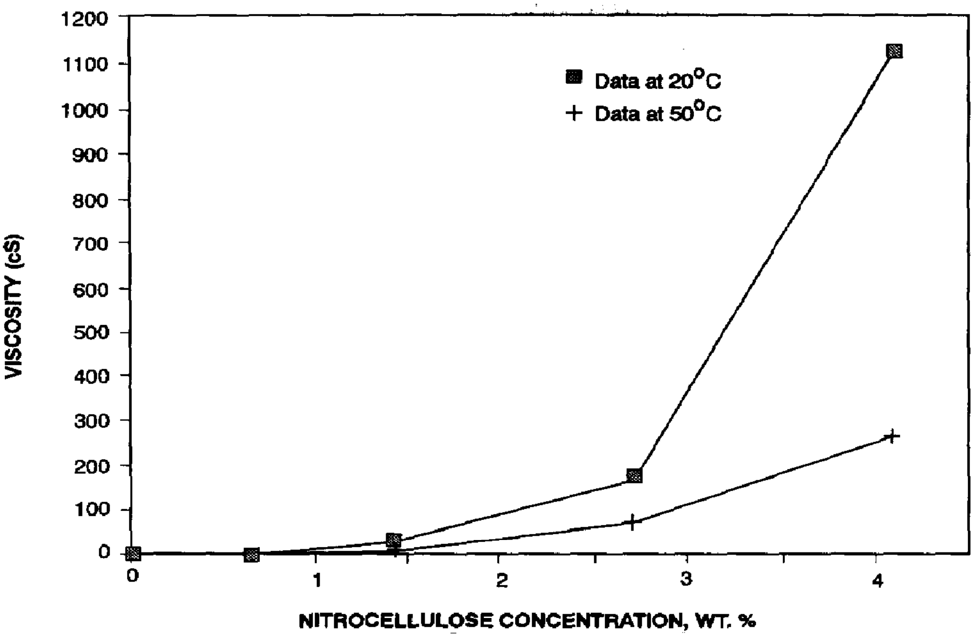

Fig. 1. The kinematic viscosities of nitrocellulose (NC)–acetone–No. 2 fuel oil solutions at 20 °C and 50 °C [6].

TABLE 2

Heats of combustion for NC, solvents, No. 2 fuel oil, and selected NC–solvent–No. 2 fuel oil solutions

Material	Heat of combustion (Btu/lb)
Blended NC (Hercules, Grade C, Type 1)	4,100
Acetone	13,229
Ethyl acetate	10,980
Butyl acetate	13,130
No. 2 fuel oil	19,500
5.8% NC–70.7% acetone–23.5% No. 2 fuel oil	14,175
1.4% NC–66.5% acetone–32.1% No. 2 fuel oil	15,115
2.4% NC–58.1% ethyl acetate–39.5% No. 2 fuel oil	14,181
2.8% NC–58.5% butyl acetate–38.7% No. 2 fuel oil	15,335

heats of combustion were measured using a bomb calorimeter according to ASTM D 240-87 standard procedure. Heats of combustion are essential for determining the thermal efficiency of equipment for producing either heat or power. These data were also required to calculate certain parameters in the economic analysis.

Compatibility of No. 2 fuel oil with NC–solvent solutions

No. 2 fuel oil was gradually added to acetone containing 1.0–7.5% NC, ethyl acetate containing 1.0–4.8% NC, and butyl acetate containing 0.5–4.4% NC. For each NC–solvent–No. 2 fuel oil solution, at the lowest concentrations of NC (0.2–1.2%), either none or only a small amount of precipitation was observed after standing for three days. For the NC–acetone–No. 2 fuel oil solutions containing 1.4–5.6% NC, significant amounts of NC precipitated from solution as a gel-like mass on the bottom of the container over the three days observation period. This precipitate was difficult to redisperse when the mixture was agitated vigorously by hand. The same general observations were also made for ethyl acetate– and butyl acetate–No. 2 fuel oil solutions containing greater than 1.2% NC.

In all cases, if the original solutions described above were placed on a reciprocating shaker on low speed, they remained free of precipitate for at least one month. Therefore, mechanical agitation would be required if batches of NC–solvent–No. 2 fuel oil solutions are stored for any period of time before being used as a supplemental fuel for an industrial combustor.

Economic analysis

Concurrent with the laboratory tests, an economic analysis of the process was also performed. First, the prices of acetone ($0.30/lb), butyl acetate ($0.43/lb), and ethyl acetate ($0.41/lb) were obtained [18]. These prices are based on railroad tank car deliveries of each solvent. Acetone is obviously the least expensive solvent for NC; furthermore, acetone was able to dissolve a greater concentration of NC (7.5%) than either butyl acetate (4.4%) or ethyl acetate (4.8%). Consequently, based on this information and the other technical data discussed earlier, acetone was determined to be the most suitable solvent for NC.

Second, the costs for combusting an NC–acetone–No. 2 fuel oil solution compared with combusting No. 2 fuel oil only were determined for two solutions containing different concentrations of NC (Table 3). Equipment and labor costs were not considered in this analysis. The data given in Table 3 clearly show that substantial additional costs will be incurred if the DOD's industrial combustors are fueled with NC–acetone–No. 2 fuel oil solutions instead of No. 2 fuel oil alone. In addition, compared to the large amount of waste propellants in the DOD's inventory, only a relatively small amount of NC-containing propellant would be disposed of per year by this process at each combustor location.

Alternative process to using NC–solvent–No. 2 fuel oil solutions as supplemental fuels

A viable alternative to combusting NC–acetone–No. 2 fuel oil solutions could be to suspend the NC in No. 2 fuel oil and use the resulting slurry as a supplemental fuel. A comparison of the costs for combusting an NC–No. 2

TABLE 3

Comparison between combusting No. 2 fuel oil versus NC–acetone–No. 2 fuel oil solutions

Combustor size (MBtu/h)	Cost to burn solution ($/h)	Cost to burn fuel oil only ($/h)	Additional cost to burn solution over fuel oil ($/h)	Amount of NC consumed, (metric tons/y)
4.2% NC, 64.6% acetone, 31.2% No. 2 fuel oil solution				
20	318	107	211	225
30	477	160	317	338
40	635	213	422	451
50	794	267	527	564
5.9% NC, 64.8% acetone, 29.3% No. 2 fuel oil solution				
20	306	107	199	323
30	459	160	299	484
40	612	213	399	645
50	765	267	498	807

TABLE 4

Comparison between combusting No. 2 fuel oil versus No. 2 fuel oil containing NC[a]

Composition	Cost to burn slurry ($/h)	Additional cost to burn slurry over fuel oil ($/h)	Amount of NC consumed (metric tons/y)
20 MBtu/h Combustor			
No. 2 fuel oil	107	—	0
5% NC–95% No. 2 fuel oil	76	−31	212
10% NC–90% No. 2 fuel oil	42	−65	442
20% NC–80% No. 2 fuel oil	−35	−142	968
30% NC–70% No. 2 fuel oil	−128	−235	1602
50 MBtu/h Combustor			
No. 2 fuel oil	267	—	0
5% NC–95% No. 2 fuel oil	189	−78	530
10% NC–90% No. 2 fuel oil	105	−162	1106
20% NC–80% No. 2 fuel oil	−88	−355	2420
30% NC–70% No. 2 fuel oil	−320	−587	4005

[a] Negative numbers represent savings.

fuel oil slurry versus No. 2 fuel oil only was performed to determine the economic feasibility of this alternative. The cost to combust NC–No. 2 fuel oil slurries with NC concentrations between zero and thirty weight percent were calculated for 20 and 50 MBtu/h combustor sizes (Table 4). Addition of NC to the No. 2 fuel oil decreases the cost to fuel a particular size combustor compared to the cost to fuel the combustor with No. 2 fuel oil only. It is also important to note that this process could dispose of greater amounts of NC per year at each combustor location than was the case for using NC–solvent–No. 2 fuel oil solutions as supplemental fuels.

Conclusions

One of the main technical difficulties of using an NC–acetone–No. 2 fuel oil solution as a supplemental fuel to fire a standard industrial combustor is that only a small amount of NC (approximately 2%) can be dissolved in the solution without the viscosity rising above the maximum value which could be handled by an unmodified oil burner. In addition, using an NC–acetone–No. 2 fuel oil solution as a supplemental fuel, besides being prohibitively expensive, would only dispose of a small amount of NC per year at each combustor location. Considering the large inventory of waste and out-of-specification NC-containing propellants in the DOD's disposal inventory, the alternative process to combust propellant–No. 2 fuel oil slurries becomes worthy of serious consideration and is currently under investigation [19]. This investigation will take into account the engineering difficulties associated with pumping slurries of this type through oil-fired burners, as well as the stack emissions expected from burning NC-containing propellant–No. 2 fuel oil slurries.

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