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Research Article

Thermochemical Analysis of Hypergolic Propellants Based on Triethylaluminum/Nitrous Oxide

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The vacuum specific impulse, density vacuum specific impulse, and solid exhaust products were examined for several propellant formulations based on the pyrophoric material triethylaluminum (TEA) using CEA thermodynamics code. Evaluation of TEA neat and mixed with hydrocarbon fuels with LOX, N_2O, N_2O_4, liquefied air, and HNO_3 were performed at stoichiometry. The vacuum specific impulse of neat TEA with N_2O is comparable to that of nitric acid with the same, but the N_2O formulation will produce slightly less solid products during combustion. Additionally, N_2O-TEA propellants have vacuum specific impulses and density vacuum specific impulses within 92.9% and 86.7% of traditional hydrazine propellant formulations under stoichiometric conditions.

1. Introduction

Nitrous oxide is a commonly used propellant in various applications ranging from aerosol cans to racing vehicles and novel rocket propellants. Because nitrous oxide may self-pressurize, there has been significant work to develop novel monopropellants using this oxidizer [1–6]. Additionally, the oxidation potential of nitrous oxide makes it an oxidizer of comparable strength to hydrogen peroxide (1.766 V and 1.776 V, resp. [7]), where hydrogen peroxide is known to ignite hypergolically with pyrophoric materials such as silane and triethylaluminum (TEA) [8, 9]. Pyrophoric materials such as TEA therefore appear to be ideal first-pass candidates for nitrous oxide hypergolic fuels. The case for these chemicals is further strengthened by the use of TEA and SiH_4 as supersonic combustion aids, since supersonic combustion requires highly flammable fuels [9]. Moreover, TEA reduces the ignition delay of hydrazine with nitrogen tetroxide [9] and ignites with air at temperatures as low as $-40^{\circ}C$ [10].

However, the mass burning rate of TEA ($0.029\,kg/m^2$-s) is much slower than short chain hydrocarbon fuels such as hexane ($0.077\,kg/m^2$-s) and isopentane ($0.103\,kg/m^2$-s) [11]. TEA diluted with a hydrocarbon fuel has mass burning rates comparable to the neat hydrocarbon, depending on mixing ratio [12]. Mixing in a hydrocarbon solvent also improves the safety of TEA by preventing its ignition with atmospheric oxygen [12, 13]. For these reasons it is important to determine not only the performance such as specific impulse (Isp), density specific impulse (ρIsp), and ignition delay of TEA with a given oxidizer, but also the effect a solvent has on the system. In the current work, Isp, ρIsp, and the amount of condensed species in the exhaust were examined. For simplicity, all specific impulse values used refer to the vacuum specific impulse, not the specific impulse at sea level.

2. Method

A thermochemical evaluation of TEA mixed with hydrocarbon solvents hexane, methanol, aniline, nitromethane, and nitropropane was performed with the oxidizers liquid oxygen (LOX), nitrogen tetroxide (NTO, N_2O_4), nitrous oxide (N_2O), liquefied air, and nitric acid (HNO_3) using the NASA Lewis Code Chemical Equilibrium with Applications (CEA2) [14]. Table 1 shows the density and molecular weight of propellant components. The binary fuels were prepared with 0, 10, 20, 25, 50, 75, and 100% TEA by mass. Each reaction was simulated at stoichiometry with a given oxidizer as determined by the method outlined in Jain et al. [15] at

Table 1: Density and molecular weight of propellant components.

Name	MW	Specific gravity (water = 1)	Ref.
Nitrous oxide	44.01	1.2228[a]	[17]
Nitrogen tetroxide/NO_2	92.01	1.443	[7]
Liquid oxygen	32	1.1905[b]	[7]
Nitric acid	63.01	1.5129	[7]
Hydrazine	32.05	1.0036	[7]
MMH	46.07	0.875	[7]
UDMH	60.1	0.791	[7]
Methanol	32.04	0.7914	[7]
TEA	114.17	0.832	[7]
Hexane	86.18	0.6606	[7]
Nitromethane	61.04	1.1371	[7]
1-Nitropropane	89.09	0.9961	[7]
Aniline	93.13	1.0217	[7]
Air	28.84	0.959[c]	[7]

[a]1.013 bars, 184.5 K [b]1.013 bars, 80 K; [c]59.75 K.

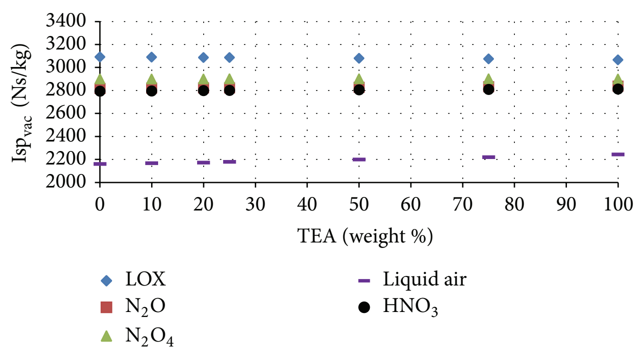

Figure 1: Isp_{vac} of TEA-hexane fueled propellants.

a chamber pressure of 2.068 MPa. The initial temperature of each fuel component was set to 25°C, with the exception of cryogenic components LOX (−185°C) and liquid air (−195°C). The heat of formation for TEA (AlC_6H_{15}) and liquid air (79% nitrogen, 21% oxygen) were manually added to CEA as −187.3 kJ/mol [16] and 0 kJ/mol. The chemistry was allowed to change through a simulated 1 : 10 expansion nozzle.

3. Results and Discussion

In terms of vacuum specific impulse (Isp_{vac}) there is little difference between the performance of nitric acid and nitrous oxide. The average difference between N_2O and HNO_3 in terms of Isp_{vac} was between 0.1% and 1.5%, depending on the solvent. Depending on the concentration of TEA, the minimum Isp_{vac} for the N_2O and HNO_3 formulations is 2794 Ns/kg for hexane, 2730 Ns/kg for methanol, 2728 Ns/kg for aniline, 2811 Ns/kg for nitromethane, and 2788 Ns/kg for nitropropane as seen in Figures 1, 2, 3, 4, and 5. The exception is methanol, where the minimum impulse was at 10% TEA when burned with HNO_3 (Figure 2). The Isp_{vac} for neat TEA with LOX, N_2O, NTO, air, and HNO_3 is 3066 Ns/kg,

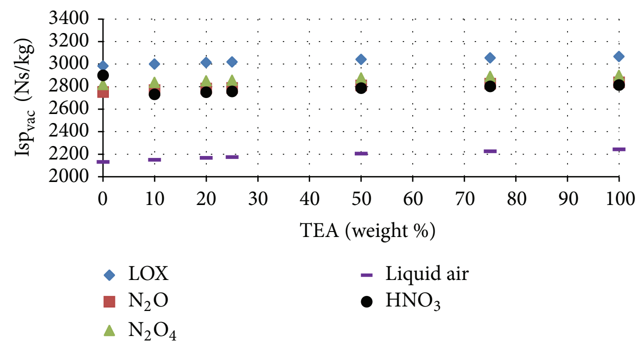

Figure 2: Isp_{vac} of TEA-methanol fueled propellants.

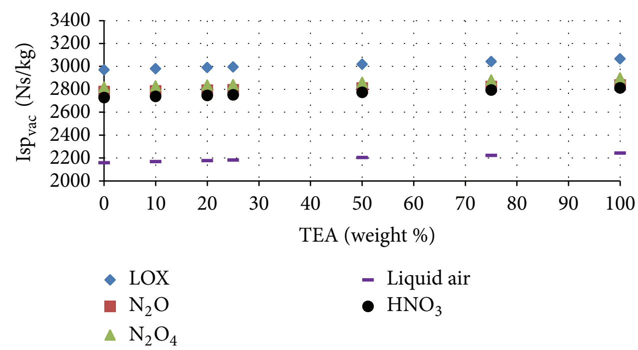

Figure 3: Isp_{vac} of TEA-aniline fueled propellants.

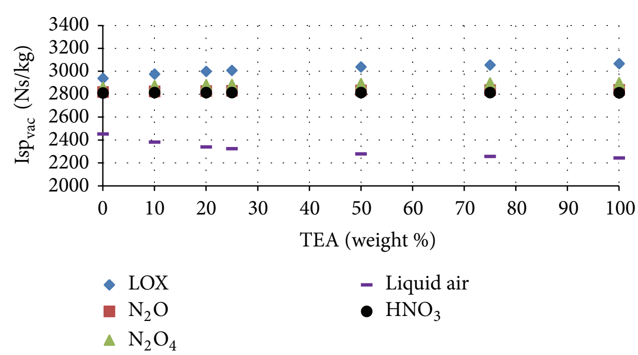

Figure 4: Isp_{vac} of TEA-nitromethane fueled propellants.

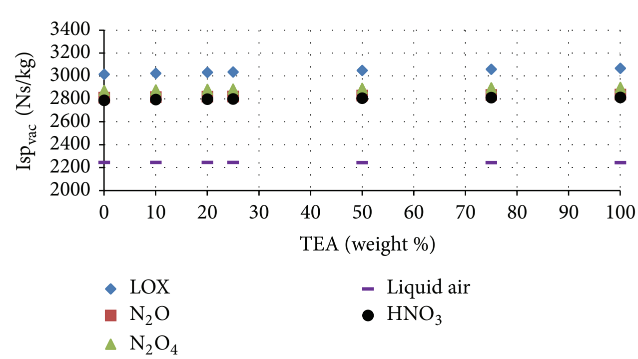

Figure 5: Isp_{vac} of TEA-1-nitropropane fueled propellants.

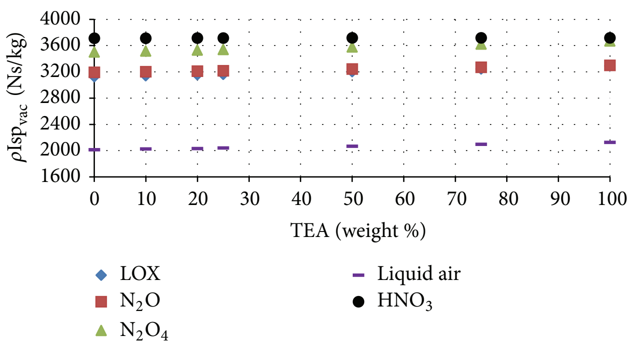

FIGURE 6: ρIsp_{vac} of TEA-hexane fueled propellants.

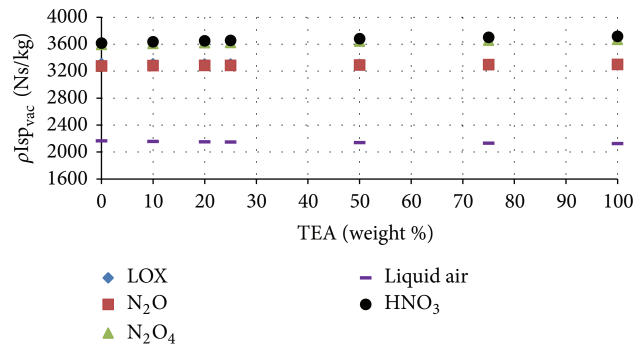

FIGURE 10: ρIsp_{vac} of TEA-1-nitropropane fueled propellants.

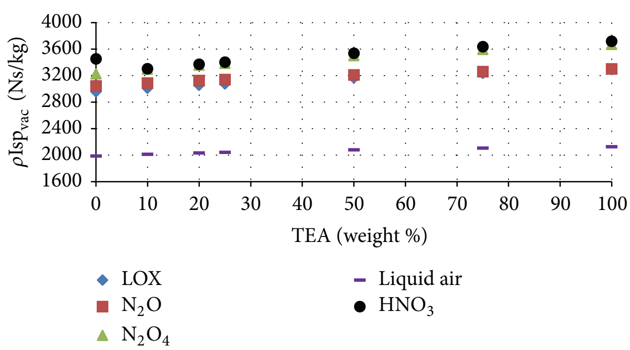

FIGURE 7: ρIsp_{vac} of TEA-MeOH fueled propellants.

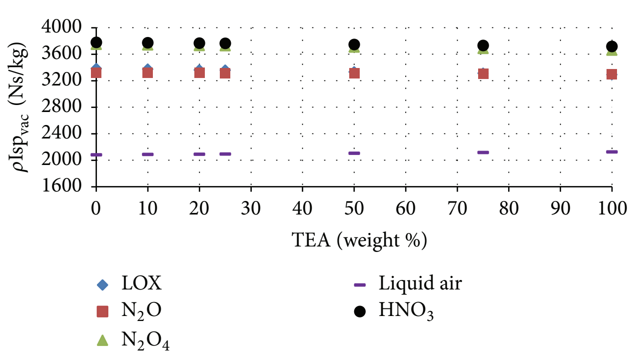

FIGURE 8: ρIsp_{vac} of TEA-aniline fueled propellants.

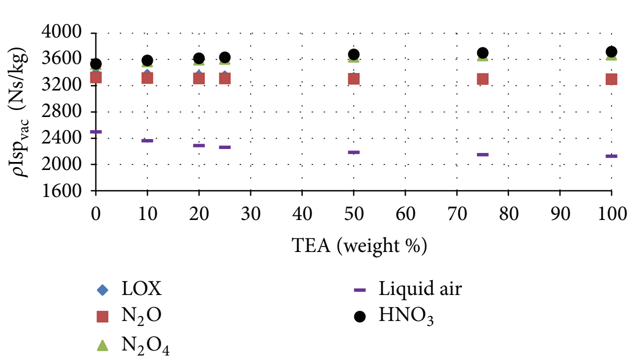

FIGURE 9: ρIsp_{vac} of TEA-nitromethane fueled propellants.

2838 Ns/kg, 2901 Ns/kg, 2243 Ns/kg, and 2813 Ns/kg, respectively. LOX and N_2O_4 formulations were predicted to have an average 6.3–9% and 1.8–2.7% greater impulse, respectively, than N_2O formulations, depending on the solvent and TEA concentration. The specific impulse of N_2O was 21.7–28.9% greater than for the liquefied air series, depending on solvent.

In a rocket, it is important to consider not only the thrust a propellant may produce, but also how large of a storage tank the propellant requires; the lower the density of the formulation the greater the volume it occupies and therefore requires a more massive storage tank, increasing the total mass of the rocket. Therefore, it is necessary to evaluate the impulse weighted by the density of the propellant. In order to maintain units, the specific gravity of each propellant (with water equal to 1.0) was multiplied to the vacuum specific impulse. Figures 6, 7, 8, 9, and 10 show nearly equivalent ρIsp_{vac} for the oxidizers LOX and N_2O, regardless of the secondary fuel. As seen in the figures, the impulses are between 3126 and 3299 Ns/kg for hexane, 3291 and 3382 Ns/kg for aniline, 3291 and 3383 Ns/kg for nitromethane, and 3277 and 3311 Ns/kg for nitropropane, depending on TEA concentration.

With the exception of aniline and methanol, the highest impulse for these formulations is for neat TEA and the least for neat fuel. Neat aniline had the highest ρIsp in its series with the lowest impulse with neat TEA. The minimum ρIsp for methanol was calculated for 10% TEA, with neat TEA having the highest impulse. Density impulses for nitric acid with fuel were comparable to those of nitrogen tetroxide with fuel for all TEA formulation besides hexane, where the nitric acid had on average 4.1% higher density impulse than nitrogen tetroxide formulations. On average, nitric acid outperformed N_2O formulations by 9.8–14.9% and nitrogen tetroxide outperforms N_2O by 8.4–12.2%. Nitrous oxide had density vacuum specific impulses 46–57.7% greater than for liquefied air propellants on average.

Generally, as with the Isp_{vac} values, the effect of the secondary fuel on the ρIsp_{vac} is minimal, suggesting that dilution of TEA will not hamper thrust characteristics assuming hypergolic ignition is achieved. This in turn will permit a minimal TEA to be utilized. This feature ought to be advantageous given the burn rates discussed in [12] where TEA burns up to one-third the rate of a hydrocarbon.

TABLE 2: Summary of Isp, ρIsp, and solid exhaust for neat TEA.

Oxidizer	Isp	ρIsp	% solid
LOX	3066	3291	11.3
N_2O	2838	3299	4.9
N_2O_4	2901	3670	8.5
Air	2243	2127	3.3
HNO_3	2813	3716	5.7

In addition to the impulse calculations, the condensed exhaust species were examined. Because solid exhaust products tend to erode the rocket nozzle, it is desirable to minimize solid exhaust products. Obviously, a fuel containing no condensable species (i.e., no aluminum) will have no solids in the exhaust; therefore the solids fraction of neat TEA with each oxidizer at stoichiometry was calculated to isolate the effect of the oxidizer on the products formed. It was observed that N_2O and air have the lowest fraction of solids loading in the exhaust as a result of the high oxidizer-fuel ratios for these formulations. A majority of the solid exhaust products were in the form of Al_2O_3, with small amounts of AlOH and $Al(OH)_3$. The highest solids fraction was calculated for LOX. Table 2 is a summary of the Isp, ρIsp_{vac}, and solids fraction. Regardless of oxidizer selection, the solids fraction is expected to be below 12%, which is significantly less than many solid rocket propellants which may contain 20% solid aluminum in the fuel. A blended fuel (TEA and hydrocarbon) would have even less solid product, depending on mixing ratio, and therefore would be expected to have retarded nozzle erosion compared to a solid rocket fuel and therefore higher combustion stability.

For comparison to conventionally used propellants based on hydrazine, the Isp_{vac} and ρIsp_{vac} of hydrazine-oxidizer systems (neat hydrazine, monomethylhydrazine (MMH), unsymmetrical dimethylhydrazine (UDMH), and Aerozine 50) are shown in Figures 11 and 12, respectively. The highest Isp for the neat hydrazines is hydrazine-LOX at 3299 Ns/kg. Once again, the lowest impulse is observed for liquid air. The highest ρIsp_{vac} is 3788 Ns/kg for hydrazine N_2O_4. With respect to only the hydrazines, N_2O produces no less than 88% of the maximum calculated impulse and 86% of the maximum ρIsp_{vac}. The worst performing N_2O system in this investigation (neat methanol-N_2O) had an Isp_{vac} within 83% and ρIsp_{vac} within 80% of the best performing hydrazine system. Neat TEA-N_2O had an Isp_{vac} within 92.9% of the hydrazine-LOX and ρIsp_{vac} 86.9% of the hydrazine-NTO formulations. In brief, TEA-N_2O propellants are expected to produce comparable impulse values to hydrazine-based propellants.

4. Conclusions

A thermodynamic analysis of potential hypergolic propellants based on TEA and nitrous oxide was performed and compared to traditional oxidizers. It was shown that nitrous oxide is comparable to nitric acid in terms of specific impulse, and in terms of density specific impulse nitrous oxide is comparable to LOX. However, the high oxidizer/fuel ratio for nitrous oxide helps to minimize the solids fraction of the exhaust, which is desirable. The effect of a secondary fuel such as hexane, MeOH, aniline, nitromethane, and 1-nitropropane was also examined and was deemed minimal. Because the thrust characteristics of a TEA fuel blend are minimally affected by the addition of a hydrocarbon fuel, a minimal volume of TEA may be utilized assuming hypergolic ignition can be confirmed. Moreover, the neat TEA-N_2O propellant produces vacuum specific impulses and density specific impulses 7.1% and 13.1% lower than traditional hydrazine propellant formulations, respectively.

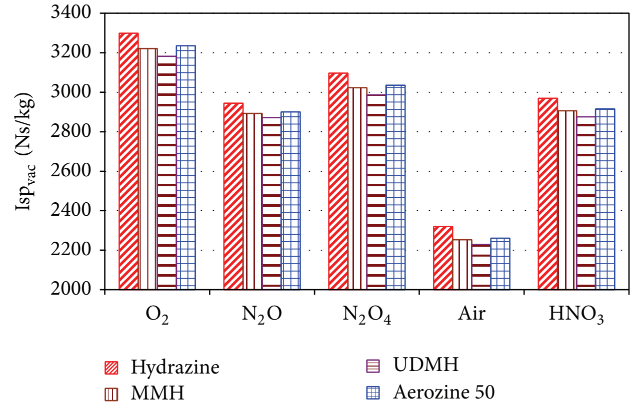

FIGURE 11: Isp_{vac} of hydrazine-based propellants.

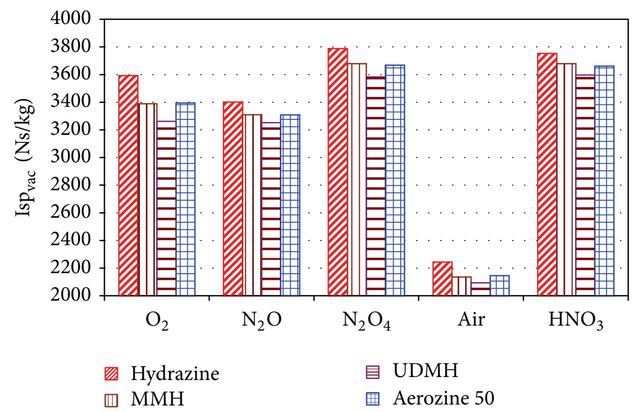

FIGURE 12: ρIsp_{vac} of hydrazine-based propellants.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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