A Thrust and Impulse Study of Guanidinium Azo-Tetrazolate as a Fuel Additive for Hybrid Rocket Motor

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Abstract: Guanidinium azo-tetrazolate (GAT) is an organic salt with a high percentage of nitrogen. GAT was mixed with the standard hybrid rocket fuel, hydroxyl-terminated polybutadiene (HTPB), in concentrations of 15% and 25% by mass. The fuel grains with the GAT additive were fired for 4 seconds with oxygen flows of 0.04, 0.06, 0.08, and 0.10 lbm s⁻¹.

Physical characteristics of the rocket were measured while firing the GAT fuels. Thrust, internal pressure, fuel mass consumed, oxygen flow rate, nozzle throat diameter, and fuel port radius were measured. Fuel regression rate, specific impulse, total impulse, and average thrust were calculated from the data.

GAT was found to increase the thrust output when added to the standard hybrid rocket fuel, HTPB. 25% GAT fuel produced approximately the same thrust as the 15% GAT fuel. Specific impulse was slightly lower with both 15% and 25% GAT fuels than with plain HTPB fuel.

Standard deviation of thrust was used as a crude measure of amplitude of oscillations during combustion. *GAT-added fuels showed a very small decrease in thrust oscillation amplitude.*

Keywords: GAT, rocket, additive, motor

Introduction

A hybrid rocket is normally powered by a solid fuel over which a gaseous or liquid oxidizer flows. The main benefit of the hybrid rocket is the ability to throttle the rocket by controlling the oxidizer flow. The fuel, usually hydroxyl-terminated polybutadiene (HTPB), is a polymer that will not burn unless a significant amount of oxygen is present. Unlike a solid rocket, the hybrid rocket may be started, stopped and restarted. This feature is especially important in the event of a problem during launch. The hybrid rocket can be shut down quickly by eliminating the oxygen source. A hybrid rocket is safer and has more flexibility than solid rockets. Hybrid rockets are also much less complex than liquid rockets, having one half of the complexity in plumbing.

The hybrid rocket facility at the University of Arkansas at Little Rock (UALR) consists of a labscale hybrid rocket motor, transducers to measure physical properties such as pressure and thrust, a control computer, and a data acquisition computer. The facility was originally built to investigate combustion instabilities and plume diagnostics. A description of the facility and history of the research at the facility may be found in previous papers.^{1,2}

The UALR hybrid rocket facility is especially suited to studies of rocket fuels and fuel additives because the fuels are fabricated on site. The UALR hybrid rocket uses a cylindrical fuel grain that is 10 in (25 cm) long with a 2 in (5 cm) outer diameter and a cylindrical port through the center with initial diameter of 0.75 in (19 mm). During combustion, gaseous oxygen flows through the fuel port and over the fuel. When a spark is supplied, the fuel is ignited and burns in the presence of the oxygen. Ignition is accomplished with a plasma generator attached to a standard automobile spark plug. A small burst of propane is used to facilitate ignition.

One useful measure of hybrid rocket fuel performance is regression rate. The regression rate of a fuel is the rate of depletion of the surface of the fuel grain during combustion. Regression for the cylindrical fuel grains is defined as



where *r* is regression rate, r_i is initial port radius, m_i is initial mass, m_f is final mass, ρ is fuel mass density, *l* is the length of the fuel grain, and *t* is the burn time.⁷

The purpose of the experiments was to determine if guanidinium azo-tetrazolate (GAT) increases the performance characteristics (regression rate, thrust, specific impulse, total impulse) of a hybrid rocket when added to HTPB fuel. GAT is an organic salt with a high nitrogen content. It is a highly energetic compound due to the energy stored in the pi bond system.

The GAT used in this project was synthesized at UALR. The process was time consuming and the initial chemical ingredients are expensive. The process contains one step in which a contact explosive, SAT, is created. Care must be taken to prevent air-drying at this step. All other steps of the process are safe. The chemical bond structure of GAT is shown in Figure 1.

Several regression rate studies have been done on guanidinium azo-tetrazolate (GAT).^{7,8,10} A preliminary study of the feasibility of using GAT



Figure 1. *The chemical structure of guanidinium azo-tetrazolate (GAT).*

as a fuel additive with HTPB was presented in 1996.⁸ The results of that study detailed solutions to problems in casting the fuel grains and the possibility of an increased regression rate. More data was needed to fully describe the properties of the GAT/HTPB fuel mixtures. A complete regression rate study was presented in 1998, verifying that GAT does increase the regression rate when used as an additive to HTPB fuel in Hybrid Rockets. Concentrations of 15%, 20%, 25%, and 30% GAT were tested. The highest regression rate was given by 25% GAT, by mass, fuel concentration. Results of this study are presented in reference 7. The increase in regression rate makes GAT a desirable fuel additive to HTPB. The next step was to determine the effect of the GAT on the average thrust, specific impulse, and total impulse of the motor.

The thrust of a rocket, F, is the reaction force experienced by its structure due to the ejection of high-velocity matter.³ Ideally, the forward momentum of the rocket is equal to the rearward momentum of the ejected gases from the nozzle. Some losses may occur due to gravity effects and air resistance in a flying rocket.

All hybrid rockets are characterized by a rapid oscillation in both pressure and thrust. There are several theories for the cause of these oscillations. One possible cause is the nature of the fuel itself. As the fuel burns, a fuel layer either liquefies or sublimates, mixes with the oxygen, and burns, forming hot gases and a char layer. The char layer is continually sloughed off out of the rocket, revealing a fresh layer of fuel for combustion. This process, called chuffing, happens many times per second. The chuffing may be a significant cause of the characteristic pressure and thrust oscillations that are seen in all hybrid rocket combustion.³⁻⁶ Another potential source for the oscillations is the oxidizer feed line. As combustion occurs in the motor, the chamber pressure increases, reducing the pressure-fed oxidizer flow, which then causes a pressure decrease. A third possible cause of the oscillations is the presence of a swirling motion of the hot gases inside the combustion chamber. This swirling motion has been imaged in the UALR hybrid rocket.² If hybrid rockets are to be employed to lift valuable cargo or human passengers into orbit, these pressure oscillations must be better understood so that they may be minimized or eliminated. The motivation for the measurements detailed in this paper is to be able to measure the thrust oscillations more accurately. With a better measurement of the amplitude and frequency composition of the oscillations, a more complete understanding of the underlying cause may be possible.

From the thrust measurement, specific and total impulse may be calculated. Total impulse, $I_{\rm T}$, is defined as the thrust force integrated over the burning time.

(2)

$$I_T = \int F dt$$

where *F* is thrust force, and *t* is time.

Specific impulse, $I_{\rm S}$, is the total impulse per unit mass of propellant consumed. Since hybrid rockets use a solid fuel and a gaseous oxidizer, mass flux of both the fuel and oxidizer must be taken into account.

$$I_{S} = \frac{\overline{F}}{\dot{m}_{o} + \dot{m}_{f}} \tag{3}$$

where \overline{F} is the average thrust, \dot{m}_{o} is the time rate

of change of the oxidizer mass, and \dot{m}_f is the time rate of change of fuel mass.

Experimental

The hybrid rocket fuel grains were cast in paper phenolic cylinders 10 in (25 cm) in length, with a 2 in (5 cm) outer (fuel) diameter and an initial port diameter of 0.75 in (19 mm). Standard fuel grains were prepared with 85% HTPB and 15% PAPI diisocyanate used as the curative agent. Additional sets of fuel grains were formed with 15% and 25% GAT by mass added to the standard HTPB and PAPI fuel mixture.

The fuel grains were fired in the UALR hybrid rocket. The gaseous oxygen flow was varied between 0.04 lbm s⁻¹ and 0.12 lbm s⁻¹. The initial and final mass, port radii of the fuel grain, and nozzle diameter were measured for each run. The runs were set for 4 or 5 seconds. However, delays in ignition caused some combustion times to be less than the set time. Pressure data were used

to determine the actual length of time between ignition and shut-down.

Because thrust is dependent upon nozzle diameter, care was taken to ensure that the nozzle diameter stayed as constant as possible throughout all of the trial runs. Since the nozzle was made of graphite, exact consistency was impossible due to ablation during the runs. The nozzle opening diameter varied from 0.28 to 0.31 in (7.1 to 7.9 mm) for the entire data sample.

An attempt was made to eliminate the nozzle ablation source of error entirely by using a hightemperature ceramic nozzle. Unfortunately, the ceramic nozzles could not withstand the hostile environment and high stresses. The nozzles shattered unpredictably during firing. Their use was discontinued for safety reasons.

The thrust measurement was made using strain gages mounted on aluminum legs supporting the rocket.^{4,5} The flexing beams were made from 2024-T81 aluminum with a yield strength of 65 kpsi. Four strain gages from Measurements Group (CEA-13-125UW-350) were placed on the two beams to form a Wheatstone bridge circuit. A two stage amplification circuit was built to collect the voltage output of the strain gages and produce a voltage between 0 and 10 V. The voltage was sampled by an A/D board at 1000 Hz.⁴

As the rocket is fired, the thrust pushes the rocket away from the plume, causing the aluminum support legs to deflect in a predictable manner. The strain experienced by the support legs is proportional to the force. The strain gage circuit output is a voltage that is proportional to the force causing the deflection. A picture of the thrust sensor is shown in Figure 2.

The thrust detector was calibrated using a hanging weight system. Known weights between 0 to 50 lb were suspended from the rocket using a pulley system to direct the force along the rocket axis. The voltage output of the strain gage conditioning circuit was collected. The calibration curve is shown in Figure 3.



Figure 2. The UALR hybrid rocket, showing the strain gage thrust sensors on the rear support legs.

Results and Discussion

The thrust as a function of time was recorded for each data run. A sample plot is shown in Figure 4. The thrust curve is characterized by several features. A small thrust was seen during the initial gas (oxygen and propane) flow from 0 to approximately 2 seconds. A sharp increase in thrust indicates the moment of ignition, followed by several seconds of rapid oscillation during the main part of the run. These oscillations are a direct result of the pressure oscillations that are normally seen in hybrid rockets. The run is then shut down as the oxygen is turned off and nitrogen gas is flowed through the rocket to quench the combustion. The flow of nitrogen is responsible for the small non-zero thrust after shutdown.

The average and standard deviation of thrust was determined for a range between the initial start-up and the shutdown of the run. The average thrusts for both the plain HTPB grain and the GAT-added grains are plotted in Figure 5 as a function of oxidizer flow rate. The standard deviations ranged from 1.5 to 2.5 lb of thrust. There was no apparent correlation between the standard deviation of thrust and the fuel content, oxygen flow, or the number of firings on each fuel grain.⁶ The amplitude of the oscillations did not increase or decrease with the addition of GAT to the HTPB fuel.

Fuel grains with 15% GAT and 25% GAT show an increase in the thrust output compared to the plain HTPB fuel thrust output, especially at all oxygen flow rates. The 25% GAT fuel does not produce significantly more thrust than the 15% GAT fuel.

Average thrust, total impulse, and specific impulse for each flow rate were determined for each firing run. Total impulse calculations were normalized for a four second run since the actual burn times varied for each run. Results are shown in Tables 1-3.

Results for specific impulse vs. oxygen flow rate are given in Figure 6. Results for total impulse vs. oxygen flow rate are given in Figure 7.

The fuel grains with 15% and 25% GAT show



Thrust Sensor Calibration

Figure 3. Calibration curve for the thrust sensor strain gage circuit.

Thrust vs. Time

HTPB/PAPI at 0.124 lbs/sec O2



Figure 4. Thrust as a function of time.

increased total impulse compared to plain HTPB fuel. The 25% GAT fuel produces more total impulse than the 15% GAT fuel, especially at the higher oxygen flow rates.

 Table 1. Data Summary for Plain HTPB

O ₂ flow/lbm s ⁻¹	<i>F</i> /lbf	$I_{\rm T}$ /lbf s	$I_{\rm S}/{ m s}$
0.049	15.55	45.92	182.29
0.064	21.87	70.12	211.45
0.082	27.69	80.45	228.42

 Table 2. Data Summary for 15% GAT

O ₂ flow/lbm s ⁻¹	<i>F</i> /lbf	<i>I</i> _T /lbf s	$I_{\rm S}/{ m s}$
0.048	18.42	54.14	181.34
0.065	25.47	72.18	204.96
0.082	33.78	99.39	214.99

Table 3. Data Summary for 25% GAT

O ₂ flow/lbm s ⁻¹	<i>F</i> /lbf	<i>I</i> _T /lbf s	$I_{\rm S}/{ m s}$
0.044	15.56	45.37	164.23
0.059	22.14	64.48	203.09
0.075	27.55	80.39	198.31
0.099	39.00	105.18	230.81

The 15% and 25% GAT fuels show a slight decrease in specific impulse. Specific impulse is the average thrust divided by the rates of fuel consumption (see equation 3). Since the average thrust of the GAT-added fuels has increased, the rate of fuel consumption must have also increased, which is consistent with the larger regression rates found previously.⁷ Ideally, a fuel additive would increase the average thrust more than increasing fuel regression rate (assuming the oxygen flow rates are unchanged), thereby increasing the specific impulse. In this study, the increase in thrust due to the addition of GAT comes at the price of faster fuel consumption and a decreased specific impulse.

The addition of GAT to the standard hybrid rocket fuel, HTPB, increases the regression rate and therefore the performance of the fuel.³ Regression rates in general are increased not only by degradation of the fuel molecules, but also by the release of energy by the azo-compounds during combustion. In addition, this compound breaks down into more reactive radicals with higher volume per unit mass. These factors contribute to a faster pyrolysis of HTPB and overall pyrolysis of the fuel.⁷

The synthesis of GAT is very time consuming, moderately expensive, and technically complex. Therefore, commercial use of GAT is unlikely at this time. In addition, environmental impact from combustion products need to be considered before using GAT in large scale hybrid motors. Since





Figure 5. Average thrust as a function of oxygen flow rate.



Specific Impulse vs. Oxygen Flow Rate

Figure 6. Specific impulse as a function of oxygen flow rate.

Total Impulse vs. Oxygen Flow (normalized to 4 second burn)



Figure 7. Total impulse as a function of oxygen flow rate.

GAT is high in nitrogen content, the formation of nitrous oxide (NO) is a concern because it is known to contribute to the formation of acid rain. Trace amounts of NO in lab-scale hybrid rocket plumes could translate into a significant amount in the plume of a large scale rocket. Spectroscopic analysis of the plume chemistry in the UALR hybrid rocket has found no evidence of NO in the plume.^{11,12}

HTPB is the standard hybrid rocket fuel. It has excellent qualities, along with some problems. The main issues are the pressure and thrust oscillations experienced by the rocket during firing. It is thought that these oscillations may be a characteristic of the fuel. We may be able to minimize these oscillations by altering the fuel with a fuel additive. An optimal fuel additive should have the following properties: thrust should be increased, regression rate should increase, specific impulse should remain the same or increase, total impulse should increase, oscillation amplitudes should decrease, and no additional harmful chemicals should be released into the atmosphere via the exhaust. The additive, GAT, in quantities of 15% by mass, is found to have most of these desirable properties. Fuels with 25% added GAT show slightly better performance. However, the increased performance may not justify the added expense of the fuel.

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Conversion from English to Metric Units

- 1 lbm = 1 pound mass = 454 gram
- 1 lbf = 1 pound force = 4.45 N
- 1'' = 1 in = 1 inch = 25.4 mm
- 1 psi = 1 pound force per square inch = 0.145 kPa