Guanidinium Azo-Tetrazolate (GAT) as a High Performance Hybrid Rocket Fuel Additive

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ABSTRACT

The purpose of this investigation was to find a high regression rate fuel suitable for use as a mixture with hydroxyl-terminated polybutadiene (HTPB). Guanidinium azo-tetrazolate (GAT) is the compound that was the focus of our research. GAT is a salt containing a high percentage of nitrogen. It has two conjugated nitrogen rings, which are negatively charged, and a positively charged component consisting of nitrogen, carbon, and hydrogen. In addition to the high-energy content of this compound, as a salt, it has a lower heat of degradation due to the ease of breaking its ionic bonds.

GAT was found to react with N100, a common curative for HTPB. An alternative isocyanate curative was found, polyisocyanate (PAPI), with which it did not react. This polymer matrix was found to be suitable for GAT. The resulting fuel grains were difficult to cast due to the rapid polymerization of the HTPB/PAPI. Once grains were cast, they required no special care in storage or firing.

The fuel grains with the GAT additive were fired for 3-second runs with oxygen flows of 0.04, 0.06, 0.08, 0.10 and 0.12 lbm/s. The regression rate of each GAT concentration was computed and plotted vs. the oxidizer mass flux on a log/log scale. The resultant curve is fit to the equation, $r = aG_o^b$*, and the quantities a and b were recorded for each curve.*

GAT was found to increase the regression rate of HTPB when it was used as an additive. The resultant pressure and thrust from firing even the highest GAT concentrations at high oxygen flows still remained within safe operating parameters of the UALR hybrid rocket motor facility.

Keywords: GAT, guanidinium azo-tetrazolate, GZT, HTPB, hybrid rocket fuel, ground testing, regression rate

Conversion from English to Metric Units.

1 lbm = 1 pound mass = 454 grams
1 lb = 1 pound = 454 grams
1" = 1 in. = 1 inch = 25.4 mm
1 psia = 1 pound per square inch = 0.145 kPa

Introduction

The hybrid rocket facility at the University of Arkansas at Little Rock (UALR) consists of a labscale hybrid rocket motor, several transducers to measure various 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.[1,2,3] Several hybrid rocket fuels and fuel additives have also been studied.

One quantization of hybrid rocket fuel performance is regression rate. The regression rate of a fuel is the rate of fuel depletion from the surface of the fuel grain during combustion, measured in inches per second. Generally speaking, regression provides a measure of how much of the solid fuel is burning for a given time. Hence an increase in regression implies an increase in thrust and output and therefore performance. Regression is relatively easy to study and quantify and is often used for basic comparisons of fuels. Since this was the first study of guanidinium azo-tetrazolate (GAT), we decided to utilize regression as a basis for comparison to plain HTPB and HTPB with other additives. Regression rate is calculated as:

$$r = \frac{\left[\left(\sqrt{\frac{m_i - m_f}{\rho \pi l} + r_i^2}\right) - r_i\right]}{t} \qquad (1)$$

where r is the regression rate (in./s); m_i is the initial fuel mass; m_f is the final fuel mass (g); r_i is the initial fuel port radius; r_f is the final fuel port radius (in.), ρ is the fuel mass density (g/in^3); l is the fuel grain length (in.); and t is the burn time (s). While the formula provides average regression rates, it also provides a good description of the motor for short burn times.

The standard fuel used in hybrid rockets is hydroxyl-terminated polybutadiene (HTPB). This fuel is characterized by a low rate of regression. Several fuel additives have been proposed and/or studied to determine if those additives increase the regression rate and improve the performance of the hybrid rocket fuel. One such additive is guanidinium azo-tetrazolate (GAT).

GAT is an organic salt with high nitrogen content. It is a highly energetic compound due to the energy stored in the π-bond system. The regression rate of this additive is large because it is a salt.[4] The large size of the ions in GAT, along with relatively low ion charge, leads to a relatively low heat of degradation. The bond structure of GAT is shown in Figure 1.[5] The authors know of no published thermodynamic data for GAT, with the exception of calculated values for computational studies.[6]

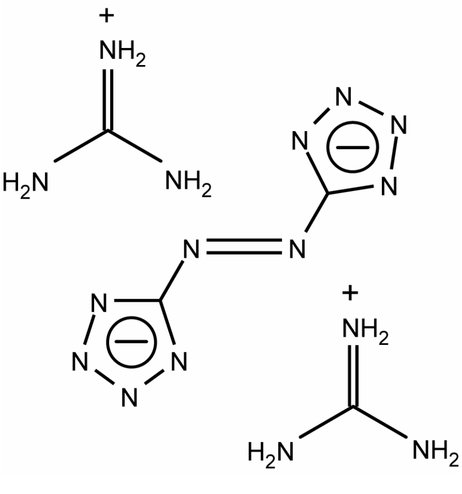

Figure 1. The bond structure of guanidinium azo-tetrazolate (GAT).

The work in this paper was done in two steps. Initially, the feasibility of using GAT as a fuel additive with HTPB was studied. The results of that study detailed solutions to problems in the casting of the fuel grains and the possibility of increased regression rate. However, more data was needed to fully describe the properties of the GAT/HTPB fuel mixtures and to determine reliable regression rates. At that point, a much larger amount of GAT was synthesized at the UALR Rocket and Combustion Laboratory. Fuel grains were cast with various percentages of GAT and a complete regression rate study was performed.

Experimental

Initial investigation of the suitability of GAT included testing using a Mettler Model DSC 20 Differential Scanning Calorimeter. Test results confirmed that GAT releases a large amount of energy and generates high quantities of gas when it reaches its thermal degradation point at about 220 °C. Additional lab studies were performed to ascertain the reactivity, if any, of GAT with HTPB resin and, N100 curative or polyisocyanate (PAPI) curative. The guanidinium component of the GAT salt was found to react with the N100 curative, releasing hydrogen gas. A test grain made with N100, HTPB, and GAT formed a foam, about one and a half times its original volume. All further polymerization and fuel grain studies were performed using PAPI as the curative, which does not react with GAT. The use of PAPI also had the effect of speeding up the curing process, so the amount of dibutyltin dilaurate was adjusted to help slow the curing process to allow proper grain casting. If the mixture sets up too quickly, voids are too easily formed.

GAT, as used in firings, was synthesized in the laboratory starting with the precursors 5-animotetrazole (Olin Chemicals) and guanidinium hydrochloride (Aldrich Chemicals). This synthesis was necessary due to the fact that there are no commercial producers. Small batches were made using standard lab glassware and following the procedure of Hiskey et al.[5] These amounts were thoroughly dried and combined with the HTPB/PAPI polymer. This mixture was then mixed for 60 seconds, and 10 microliters of dibutyltin dilaurate was added to catalyze the polymerization process. The grains had to be cast as quickly as possible because the mixture became unpourable within ten minutes. Initially, each grain contained 15% GAT, 1% graphite (added as an opacifier), with the balance made up of a polymer base containing 85% HTPB and 15% PAPI.

Rocket fuel grain casting for the labscale system is accomplished using a 10-inch paper phenolic casing, sized to fit the inside of the combustion chamber (2 in). A mandrel is used to form the cylindrical grain that results in a 0.75-inch diameter bore. Firings of the GAT/ HTPB mixtures were made using our labscale hybrid rocket system, which has a 2 × 10-inch thruster, capable of operating at pressures to 500 psi and supporting oxygen flows to 0.16 lbm/s. This system is computer controlled and is instrumented for pressure. Additional details on the Hybrid Rocket Facility may be found in a previous papers.[1,2]

GAT was mixed in several percentages by mass with HTPB, and PAPI was used as the curative agent. Fuel grains were prepared in 15, 20, 25 and 30% by mass concentrations of GAT. Graphite was added to the fuel grain mixture at 1% by mass concentration as an opacifier. The remaining fuel composition was again a mixture of 85% HTPB and 15% PAPI.

The fuel grains were fired in the UALR hybrid rocket. To ascertain the magnitude of the difference that the addition of GAT would have, an initial set of six firings at 0.06 lbm/s oxygen flow were performed. These firings were used to set the conditions for a test matrix for data reporting. The gaseous oxygen flow was then varied between 0.04 and 0.12 lbm/s in 0.02 lbm/s increments. Each percentage of GAT fuel was fired at each of the oxygen flow rates, for a total of 20 firings. The mass and the initial and final port radii of the fuel grain were measured for each run. The rocket was fired for three seconds per run. Regression rate was calculated for each run using equation 1. Results are presented in Table 1.

For each percentage GAT fuel, regression rate r vs. oxidizer mass flux G_o was plotted on a log/log scale. The five data points for each percentage GAT were plotted and fit to the equation

$$r = aG_o^b \tag{2}$$

Table 1. Regression Rate Results.

Fuel Run	O_2 Mass Flux, G_o (lb/in.^{2}s)	Regression (in./s)
0% GAT		
1	0.0565	0.034
2	0.102	0.039
3	0.113	0.038
4	0.115	0.030
5	0.123	0.027
15% GAT		
1	0.057	0.032
2	0.068	0.028
3	0.090	0.031
4	0.101	0.040
5	0.197	0.049
20% GAT		
1	0.072	0.037
2	0.099	0.044
3	0.138	0.054
4	0.156	0.051
5	0.178	0.055
25% GAT		
1	0.073	0.038
2	0.089	0.034
3	0.100	0.045
4	0.138	0.043
5	0.156	0.053
30% GAT		
1	0.049	0.029
2	0.083	0.036
3	0.097	0.047
4	0.110	0.039
5	0.150	0.055

Fit results for the regression rate calculations are presented in Table 2, and the curves are shown in Figures 2 to 5.

Table 2. Fit Results for the Regression Rate Calculation $r = aG_o^b$.

Fuel	a	b
15% GAT	0.099	0.435
20% GAT	0.113	0.416
25% GAT	0.107	0.418
30% GAT	0.156	0.559

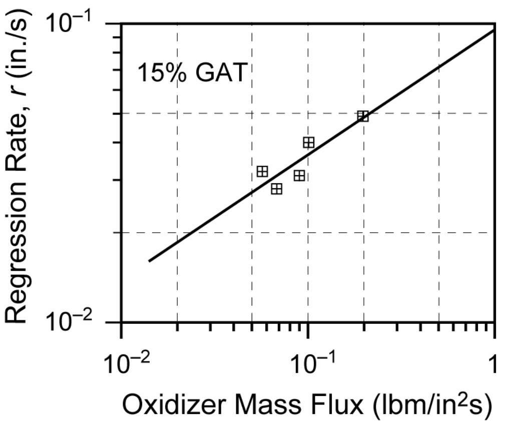

Figure 2. 15% GAT regression rate.

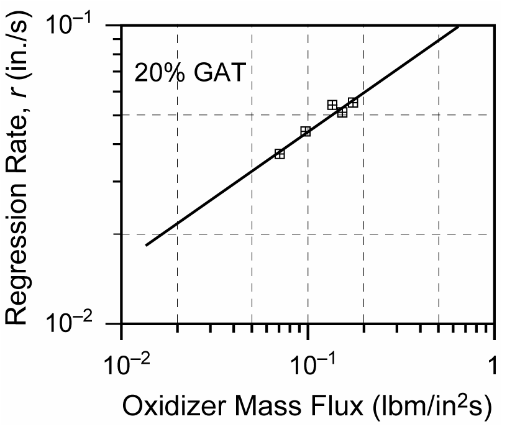

Figure 3. 20% GAT regression rate.

Results and Discussion

The addition of GAT to the standard hybrid rocket fuel, HTPB, increased the regression rate and therefore the performance of the fuel. Regression rates in general are increased not only by degradation 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. Casting of GAT grains was somewhat difficult. Due to the relatively fast polymerization of the HTPB/PAPI, thoroughly mixing the catalyst into the fuel creates small bubbles. These generally do not have time to escape before the polymer solidifies. This problem can be overcome by investigating alternative HTPB/PAPI base polymer mixes to slow the polymerization process. Otherwise the resulting GAT fuel grains were satisfactory for storage and labscale hybrid testing, with the GAT dissolving completely at the percent concentrations tested in this study.

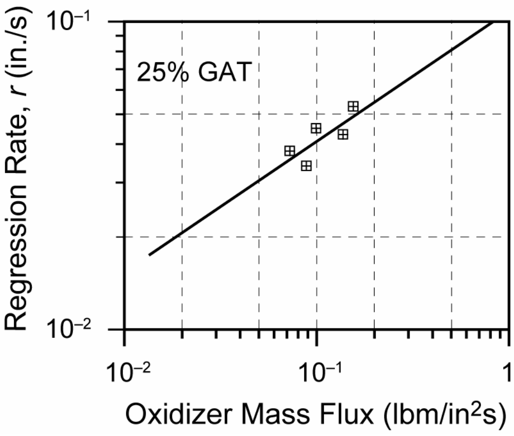

Figure 4. 25% GAT regression rate.

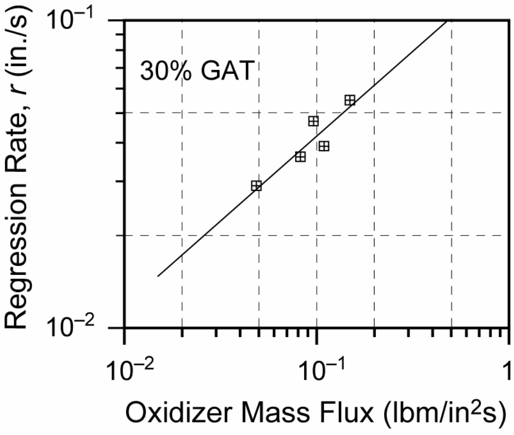

Figure 5. 30% GAT regression rate.

Our first firing of GAT was performed at a 20% by mass concentration level, but high-pressure conditions (over 575 psi), felt to be due to a high regression rate, caused a system safety shutdown. Another five test firings were conducted on fuel grains using a lesser percentage GAT additive (15% by mass concentration), and suitable data was obtained for these to indicate safe firing parameters. We had expected this firing to generate perhaps 300 psi. Another five test firings were conducted on 15% by mass concentration of GAT fuel grains, and suitable data was obtained for these to indicate safe firing parameters. These tests indicated the conditions for the test matrix that resulted in Table 1. Tables 1 and 2 show that the addition of GAT increases the performance as measured by fuel port regression for a set oxygen mass flux. See Figure 6 for a comparison of the various percentages of GAT. This increase can be as much as 150% when compared to the firing of plain HTPB grain. For example, a "plain HTPB" fuel grain (one containing no regression additives) in previous work showed a regression rate of 0.0363 in./s for an oxidizer mass flux of 0.1562 lbm/(in.^{2}·s).[2]

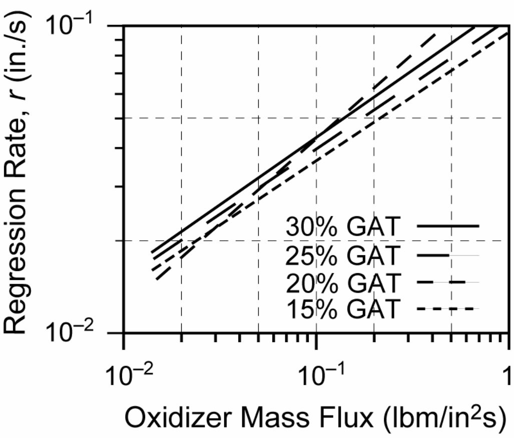

Figure 6. Comparison of all GAT firings reported. Note the increase in regression rate for each percentage increase (with the exception of the 20% line).

Utilization of GAT/HTPB fuel therefore shows significant promise when compared to plain HTPB.

It is felt that the addition of GAT gives an increase in regression due to several factors. One is that GAT has a lower degradation temperature and takes less energy to pyrolyze than HTPB. However, GAT releases significantly more energy during its degradation than HTPB and does so at the fuel surface. This results in even more fuel breakdown, including both GAT and HTPB. GAT should break down into highly reactive radicals with a high gas volume per unit mass. This high volume tends to sweep the fuels from the degradation zone into the combustion zone more quickly than the relatively lower volume gases produced by HTPB and related fuels. The properties of GAT may also result in the physical ejection of fuel particles into the burn zone of the chamber and the plume during firing, adding to a higher regression rate.

A possible concern with using GAT as a fuel additive is the increased risk of environmentally dangerous compounds, such as NO, released in the plume. Preliminary UV-Vis absorption data does not show significant amounts of NO in the plume of the fuel grains fired in this study.[7]

Conclusions

GAT has been shown to increase the regression rate of HTPB fuel in hybrid rockets as much as 150% when compared to plain HTPB. However, the synthesis of GAT is time consuming and difficult on the lab scale. Also, the components needed to synthesize GAT are moderately expensive. This expense will be diminished on a production scale due to buying the chemical components in bulk and streamlining the production process.

Acknowledgments

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References

1) R. B. Shanks and M. K. Hudson, "The Design and Control of a Labscale Hybrid Rocket Facility for Spectroscopic Studies", AIAA Paper No. 94-3016, June 1994.

2) R. Shanks and M. K. Hudson, "A Labscale Hybrid Rocket Motor for Instrumentation Studies", *Journal of Pyrotechnics*, No. 11 (2000) pp 1–10.

3) M. K. Hudson, R. Shanks, D. Snider, D. Lindquist, "UV, Visible, and Infrared

Spectral Emissions in Hybrid Rocket Plumes”, *International Journal of Turbo and Jet Engines*, Vol. 15 (1998) pp 71–87.

4) G. Lengelle, B. Fourest, J. C. Godon, and C. Guin, “Condensed Phase Behavior and Ablation Rate of Fuels for Hybrid Propulsion”, AIAA Paper No. 93-2413, June, 1993.

5) M. Hiskey, N. Goldman, and J. R. Stine, “High-Nitrogen Energetic Materials Derived From Azo-Tetrazolate”, unpublished manuscript, Los Alamos National Laboratory, January, 1996.

6) C. Chen, M.H. Liu, S.R. Cheng, and L.S. Wu, “Theoretical Study of the Inter-Ionic Hydrogen Bonding in the GZT Molecular System”, *Journal of the Chinese Chemical Society*, 50 (2003) pp 765–775.

7) M. W. Teague, J. R. Welborn, T. M. Flelix, M. K. Hudson, and J. Willis, “UV-Vis Absorption as a Diagnostic for NO in Rocket Plumes”, *International Journal of Turbo and Jet Engines*, Vol. 13 (1996) pp 211–21.

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