Effect of an Fe-Based MOF Additive on the Burning Rate of AP/HTPB Composite Propellants

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1 Introduction

For years, additives have been used to modify propellant properties, such as ignition delay time and burning rate [1,2]. Metallic additives, such as aluminum, enhance burning rate and specific impulse in composite solid propellants. Recently, metal-organic frameworks (MOFs) have gained attention for their unique structures, which may improve burning rates, lower sensitivity, and increase heat of combustion [3]. MOFs consist of an inorganic metal group and an organic molecule called a linker, giving them high surface area and tunable porosity, ideal for catalysis in combustion. Studies have explored MOFs in propellants, such as a copper-based MOF in an AP/HTPB propellant, which increased the burning rate but slightly reduced specific impulse [3]. Another study with a graphene-ferrocene-based MOF also found increased burning rates [4]. These studies suggest MOFs could enhance propellant burning rates and offer adjustability and higher heat of combustion. This study further investigates the performance of MOF-based propellants and compares their burning rates to baseline formulations, with emphasis on an Fe-based MOF additive. Presented first is an overview of the experimental setup and methodology, followed by a presentation of the burning rate results for both baseline and MOF-enhanced propellants.

2 Experimental Configuration

This study analyzed the combustion properties of a novel iron-based MOF, iron (III) oxo acetate perchlorate hydrate ($C_{12}H_{24}Fe_3O_{16} \cdot ClO_4 \cdot xH_2O$), chosen for its potential as a catalytic additive in solid propellant formulations. Iron is a common catalyst in composite solid propellants (CSPs), improving combustion properties like burning rates and specific impulse. The FeMOF also contains a perchlorate compound, a known oxidizer in combustion processes. The FeMOF was incorporated into baseline formulations with ammonium perchlorate (AP) as the oxidizer, R45-M hydroxyl-terminated polybutadiene (HTPB) as the fuel-binder, and isophorone diisocyanate (IPDI) as the curative [5,6]. Various fuel matrices were synthesized to analyze the FeMOF's combustion properties, considering the additive type, percentage, AP particle sizes, and mixing practices. The FeMOF was compared to baseline mixtures with no additives and those containing iron (III) oxide (Fe_2O_3), a common CSP additive. Additive percentages were varied, as higher percentages generally improve burning rates. AP particle sizes were either monomodal (200 µm) or bimodal (70:30 distribution of 200 to 20 µm). Mixing practices included using a mortar and pestle to achieve finer particle sizes for better distribution. All formulations are detailed in Table 1.

Table 1. Test matrix of AP/HTPB formulations to characterize FeMOF performance.

Mixture	Additive	Additive%	AP Distribution	Additional Information
Monomodal Baseline	-	0.0	Monomodal	-
Bimodal Baseline	-	0.0	Bimodal	-
1.0% Fe_2O_3 Monomodal	Fe_2O_3	1.0	Monomodal	-
2.4% Fe_2O_3 Monomodal	Fe_2O_3	2.4	Monomodal	-
1.0% FeMOF Monomodal	FeMOF	1.0	Monomodal	-
2.4% FeMOF Monomodal	FeMOF	2.4	Monomodal	-
5.0% FeMOF Monomodal	FeMOF	5.0	Monomodal	-
2.4% FeMOF Bimodal	FeMOF	2.4	Bimodal	-
2.4% FeMOF Monomodal Deagglomerated	FeMOF	2.4	Monomodal	Utilized Mortar & Pestle on FeMOF Before Incorporation
2.4% FeMOF Bimodal Deagglomerated	FeMOF	2.4	Bimodal	Utilized Mortar & Pestle on FeMOF Before Incorporation

The mixtures were prepared with 80% solids loading and a 10.44:1 mass ratio of HTPB to IPDI. Components were added in order of decreasing particle size, followed by liquid ingredients. The materials were hand-mixed for 5 minutes, then vibrationally mixed using a Resodyn LabRAM II mixer, achieving homogeneous blending. The mixture was then vacuumed for one hour to remove air bubbles. After vacuuming, the mixture was cast into ¼"-diameter Teflon tubing and cured at 65°C for one week. Sample mass and length were measured, and the densities were compared to theoretical maximum densities (TMD) to assess homogeneity. Five, one-inch-long propellant strands were made for each mixture and were evaluated in a strand burner at pressures from 3.4 to 15.5 MPa (500 to 2250 psi). The burning rates were determined based on time delays in pressure profiles. Further details are provided by Carro et al. [9].

3 Experimental Results

The original motivation for this study was to analyze the relationship between the FeMOF additive in comparison to CSPs which contained either no additive or an Fe_2O_3 substitute. To accomplish this, 1% FeMOF and Fe_2O_3 were added to a monomodal, 80% solids loading propellant by mass. The subsequent samples were burned and compared to a batch that was strictly 80% AP and 20% HTPB and IPDI. The burning rate results are depicted in Fig. 1.

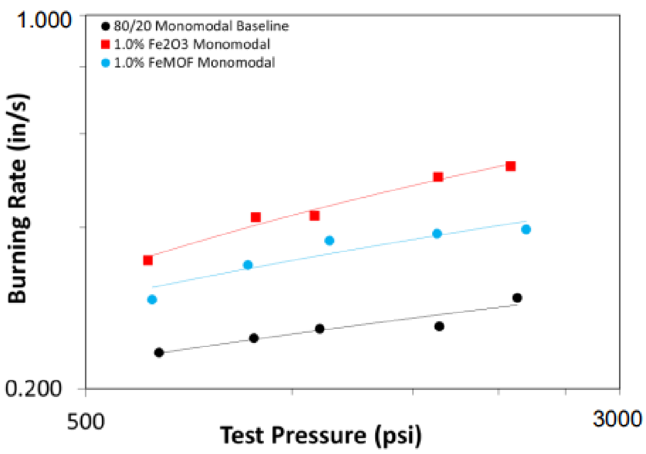

Figure 1. Monomodal comparison of 1% mass FeMOF, $\boldsymbol{Fe_2O_3}$ in relation to baseline 80/20 AP/HTPB.

While the FeMOF demonstrated slower burning behavior comparatively to the Fe_2O_3 batch, it did greatly outperform the baseline formulation with no additive. This positive result indicates that the selected MOF sufficiently serves as a combustion catalyst for composite solid propellants. Following this conclusion, more fuel matrices were synthesized to analyze the impact of implementing higher concentrations of FeMOF into the samples. For this, formulations including 1%, 2.4%, and 5% FeMOF by mass were manufactured and are subsequently compared to the previously created baselines in Fig. 2.

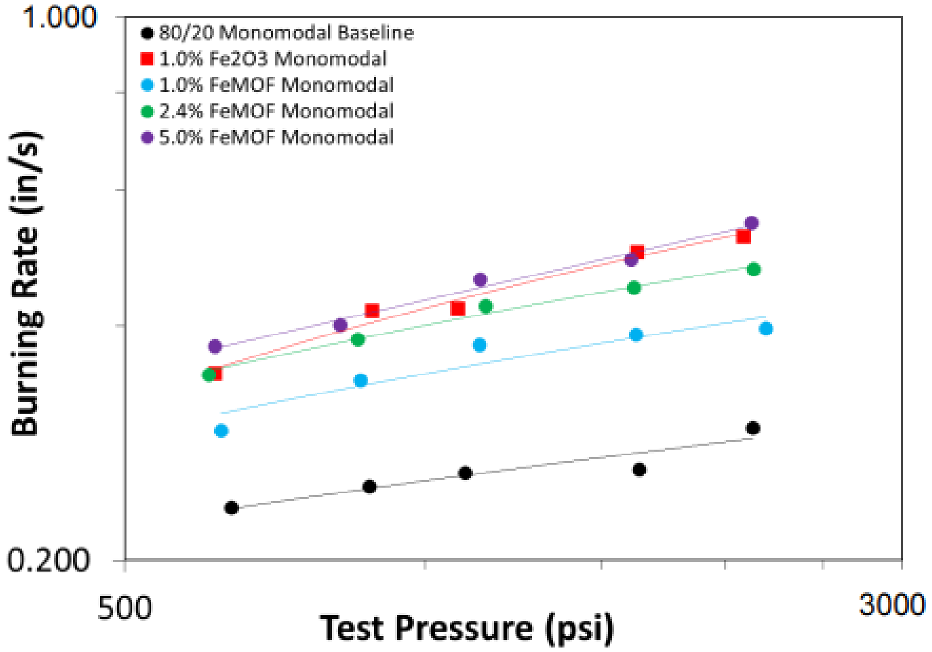

Figure 2. Monomodal comparison of 1%, 2.4%, and 5% FeMOF formulations in relation to previous baseline mixtures.

This round of testing provided insight into the positive correlation between the percentage of MOF additive and the increase in burning rate behavior. There was a steady increase in the speed of the burn proceeding from the 1% batch to the 5% batch. Subsequently, the batch with the highest mass of FeMOF slightly outperformed the Fe_2O_3 batch, indicating that the FeMOF could potentially serve as a desirable combustion catalyst even when compared to some more established transition metals.

Following the study of the correlation between concentration and burning rate, the next area that was analyzed was the impact that varying AP particle distribution would have on the performance of the FeMOF. To accomplish this, four batches were manufactured: one batch being a monomodal baseline, a second being a bimodal baseline, a third being monomodal with 2.4% FeMOF, and a final batch being bimodal with 2.4% FeMOF. All formulations were burned in the constant-volume strand burner and are compared utilizing Fig. 3.

This round of tests showed that integrating multiple sizes of AP particles into a formulation correlated with an increase in burning performance. This is consistent with literature such as Dillier et al., which reiterates the idea that integration of finer AP particle sizes into a more coarse distribution can assist in elevating burning rate performance [10]. This phenomenon remains consistent with the current FeMOF study, although its impact is less noticeable than its baseline counterpart.

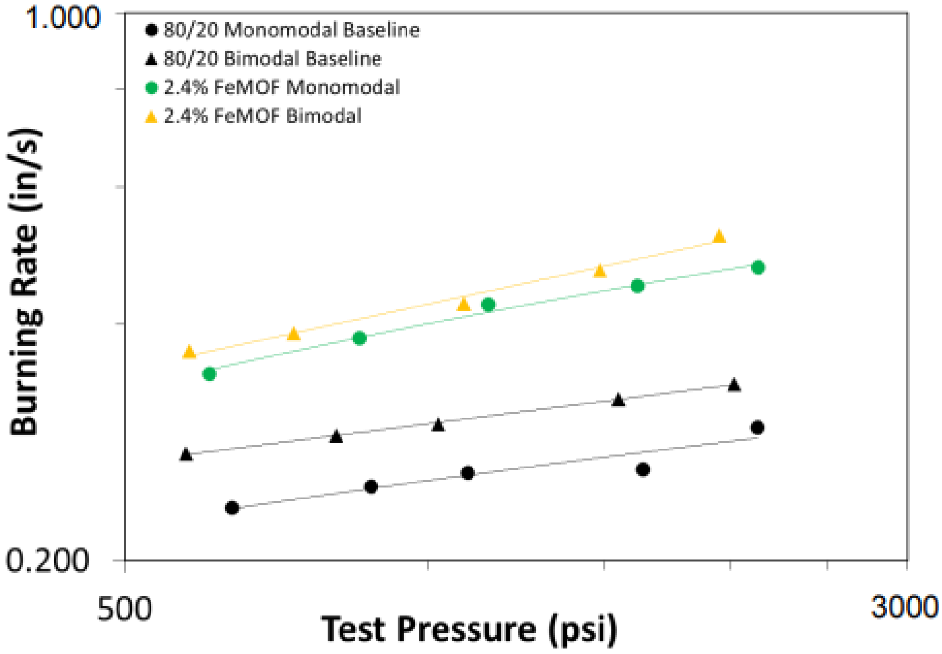

Figure 3. Comparison between monomodal and bimodal mixtures, including baselines and FeMOF formulations.

While analyzing the effects of particle distribution on burning rate performance, another parameter was determined to be desirable to investigate. Although the effects of AP particle size on combustion performance were well studied and documented, it also became crucial to understand how this specific additive particle size and distribution impacted these parameters. For all previous mixtures, the FeMOF was mixed into solid propellant formulations utilizing the particle size received from MilliporSigma. This leads to several inconsistencies and agglomerations in the additive, which could negatively impact combustion performance. To resolve this, two formulations were developed; the first utilizing 2.4% of the FeMOF with no additional mixing practices incorporated, while the second involved utilizing a mortar and pestle to grind the FeMOF into a finer and evenly distributed particle size before being mixed into the CSP. The subsequent batches were burned and compared to determine the true impact on burning rate performance. For this test, “2.4% FeMOF Deagglomerate Monomodal” refers to the batch that underwent a mortar and pestle before incorporation, while “2.4% FeMOF Monomodal” references the batch that utilized the additive as it was received from the manufacturer.

As hypothesized, the initial particle distribution received from the manufacturer had an adverse impact on the combustion performance of the CSP. The batch that was manipulated to remove agglomerations and inconsistencies greatly outperformed its baseline counterpart. This outcome is supported by the conclusion that the more homogeneous the additive and fewer agglomerations, the more readily it can be integrated into the mixture, supporting better catalytic behavior. Following this conclusion, a composite study between additive particle distribution and AP particle distribution was conducted. The relationship between solid particle distribution and burning performance was investigated using a combination of bimodal, monomodal, agglomerated, and deagglomerated mixtures. The results of this study are demonstrated in Fig. 4.

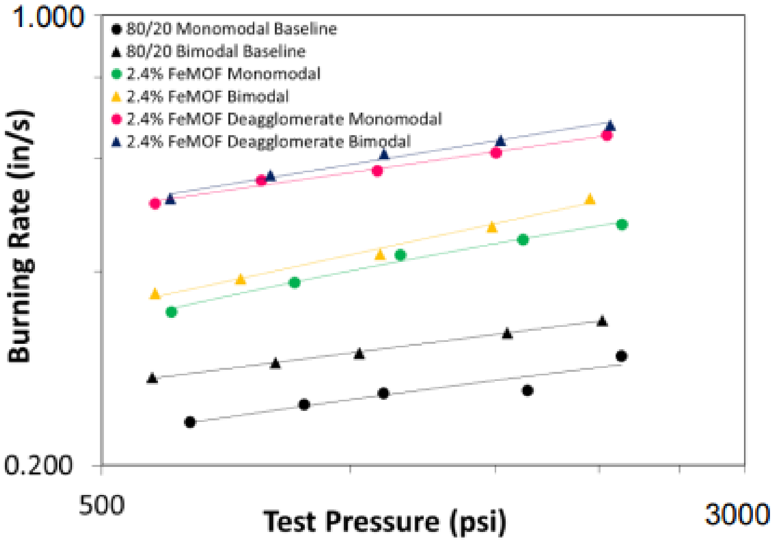

Figure 4. Comprehensive study of the correlation between burning rate performance and particle distribution of both AP and FeMOF additive.

The results of this study supported conclusions previously demonstrated. Firstly, a bimodal AP distribution provides slight increases in burning rates compared to monomodal distributions. Additionally, creating a more uniform and homogeneous additive particle profile positively contributes to increased burning performance. In combination, these two parameters complement each other, resulting in the formulation with reduced additive agglomerations and a bimodal AP distribution performing the best in comparison to other mixtures.

Following the study of these individual parameters, a comprehensive plot was developed with all formulations tested throughout the study, as presented in Fig. 5.

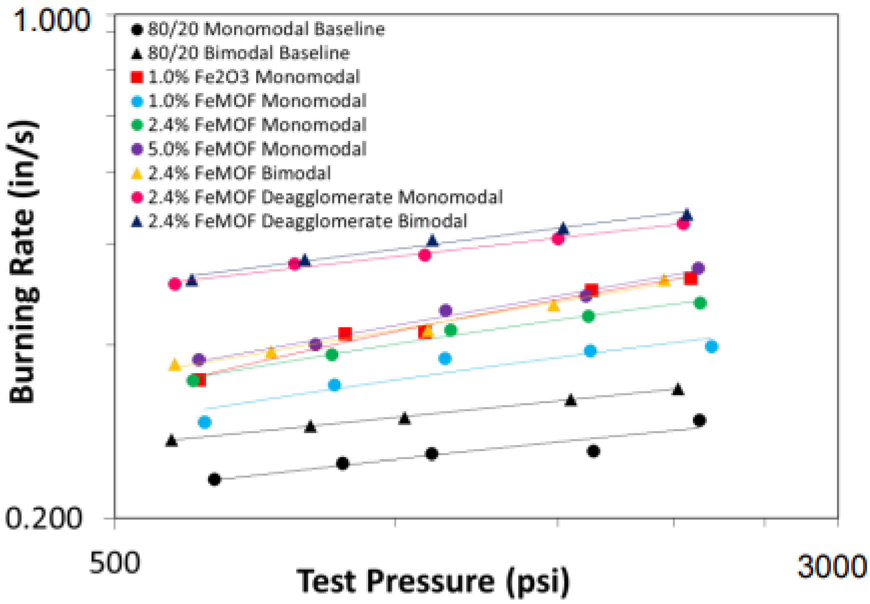

Figure 5. Comprehensive burning rate results for all mixtures characterized throughout the study.

4 Conclusions

In this study, a novel Iron-Perchlorate MOF was investigated as a combustion catalyst for AP/HTPB-based composite solid propellants. To characterize the performance of this MOF, the burning rate of varying formulations was analyzed utilizing a constant-volume strand burning apparatus. Through established mixing practices, formulations were developed to analyze the impacts of FeMOF implementation, additive concentration, AP particle size distribution, and additive particle distribution on burning rate performance. These parameters were successfully investigated, and several conclusions were drawn. Firstly, the novel FeMOF sufficiently elevated burning rates compared to a baseline counterpart, which included no catalytic additives. Additionally, integrating a higher percentage of additive mass positively correlated with an increased burning rate. Likewise, the implementation of finer AP particle size in a coarse AP mixture demonstrated higher burning rates, which agrees with previously established literature. Finally, it was concluded that developing a more homogeneous particle size of the FeMOF and reducing agglomerations throughout the mixture positively impacted burning rate performance.

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