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STUDY OF THE CATALYST ON THE REGRESSION RATE OF HTPB-BASED FUEL GRAIN FOR HYBRID ROCKET PROPULSION USING A 2D SLAB BURNER

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Abstract.
Classic fuels used in hybrid propulsion are at a disadvantage due to their low rate of regression when compared to the class of liquefying fuels. Classic fuel grains based on hydroxyl-terminated polybutadiene (HTPB) are crosslinked, therefore, they present a high resistance to sublimation and burning, which is one of the main factors that influences their low rate of regression., several research groups have been studying ways to improve the rate of regression of HTPB-based fuels, such as by the addition of catalysts or ballistic modifiers. Thus, this work consists of a preliminary study to evaluate the influence of the thermal degradation catalyst copper acetylacetonate (CuAA) on the regression rate of HTPB-based fuel grains using a 2D slab burner with a quartz window on a laboratory scale. The results show that the presence of the CuAA catalyst caused a major increase in the fuel grain regression rate when compared to the sample without catalyst. In addition, the presence of CuAA increased the grain sensitivity to the variation of the oxidant mass flux.
Keywords: Aerospace engineering, hybrid rocket propulsion, regression rate, HTPB, 2D slab burner

1. INTRODUCTION

After some catastrophic failure events on solid rocket motors in the American Space Program, including the Space Shuttle Challenger accident in 1986, the National Aeronautics and Space Administration (NASA) began a search for alternatives to the solid boosters of Space-Shuttle, thus rescuing the study of the hybrid rocket motors (Sackheim, Ryan and Threet, 2001). Hybrid rocket systems have the potential to become of strategic interest in the aerospace industry due to its low cost, safety, thrust controllability and throttling (Karabeyoglu et al., 2011).

Returning as a subject of study in the 1990s, the hybrid propulsion was initially developed in the 30s, when the Russian H. Oberth created a hybrid rocket motor with graphite rods as a fuel grain and liquid oxygen as an oxidizer for displaying a movie premiere. The motor could have been one of the pioneers in hybrid propulsion systems had it not been for a motor failure due to resistance to sublimation and burning of the graphite grains (Altman, 1991). Since then, improvements in the fuel grain burning efficiency have been studied (Karabeyoglu, Cantwell and Altman, 2001). The regression rate, or the spatially averaged burning rate of the solid fuel grain, is the most significant characterization parameter of a hybrid rocket motor, and it depends on several parameters, like the oxidizer mass flux, chamber pressure, and axial distance along the grain (Zilwa et al., 2004). Usually, the improvement in the regression rate incorporates new problems to the motor, such as, for example, poorer mechanical properties of the fuel grain and greater ablation in the nozzle (Wang et al., 2020).

In classical configurations, crosslinked polymeric fuel grains usually deliver a lower regression rate as it can be seen in hybrid rocket motor applications when hydroxyl-terminated polybutadiene (HTPB) is used as pre-polymer and isophorone diisocyanate (IPDI) as cross-linker for instance. The regression rate is associated with the resistance to degradation and vaporization from the HTPB-based polymer matrix and it presents lower results when compared to the liquefying fuel grains (Karabeyoglu, Altman and Cantwell, 2002; Gascoin, 2012, and Marxman, 1965). For HTPB-based fuels, the regression rate is normally improved by adding in the formulation energetic fuels (micro/nano-sized metals, mechanically activated powders, hydrides) (DeLuca et al., 2013) and oxidizers (as ammonium perchlorate) (George et al., 1998), and including high thermal conductivity and high radiation absorption materials as carbon nanotubes and opacifiers. Recently, some research groups have observed that some transition metal elements can catalyze the thermal decomposition of polymers (Cardoso et al., 2019; Pimont et al., 2019, and Yu et al., 2021). In this context, the copper acetylacetonate (CuAA) catalyst, Figure 1, was tested in order to verify its effectiveness in the degradation and burning of the HTPB-based fuel grain and its sensitiveness to the variation of the oxidant mass flux (GOX).
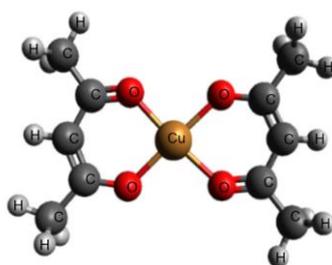

Figure 1. Molecular structure of the Copper acetylacetonate (CuAA).

For that, a 2D slab burner with a quartz window was used aiming the visualization of the combustion process on the fuel surface, as well as the analysis of temporal and spatial behavior of the regression rate so as to observe how the addition of CuAA to the HTPB grain influence the rate of regression during the burning. This approach, as opposed to the widely used end-point method, can identify transient phenomena, anomalies, as well as temporal and spatial behavior. In addition, it is reliable considering preliminary studies. For the visualization methodology adopted in this work, the combustion port mean length over the burn time.

2. EXPERIMENTAL SETUP

2.1 Fuel-grain preparation

In order to study the influence of the CuAA catalyst on the regression rate of fuel grain based on HTPB, two samples were processed, one of HTPB-based polyurethane without the catalyst and the other containing 3% m/m of the CuAA catalyst. In the fuel grain processing, the following reagents were used: HTPB (Evonik, lot TE206571-1), as a prepolymer, isophorone-diisocyanate (IPDI, Hülls, lot 11/0016), as a cure agent and dioctyl-adipate (DOA, Scandiflex, lot 712040004) as a plasticizer. The CuAA catalyst was synthesized and characterized according to (Cardoso et al. 2019).
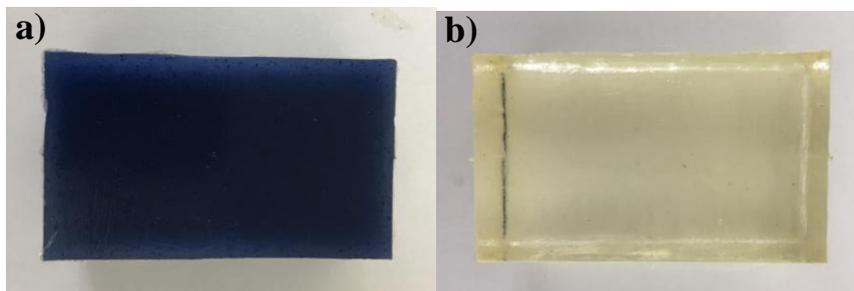

Figure 2. HTPB-based fuel samples a) with the CuAA catalyst, and b) without catalyst.

The samples were processed in a 250 mL beaker, since the sample for the current analysis does not require large quantities. First, the HTPB resin and the plasticizer were added, followed by the addition of the catalyst to the sample for those samples that needed the catalyst for the study. After a pre-mix of these reagents, the curing agent was added and mechanically mixed with the aid of a spatula until the mixture presented a homogeneous appearance. The sample was then placed under vacuum to remove bubbles and then loaded into the molds and taken to an oven at 60°C, where they

were kept for 7 days for the curing process to take place. After the curing process, the samples were cut in dimensions 59X18.4X20 mm.
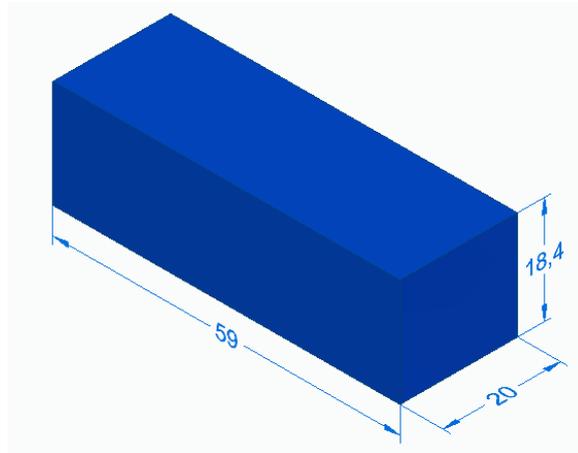

Figure 3. Dimensions in millimeters (mm) of the fuel grain samples.

2.2 Combustion Chamber and Feed Line System Configuration

The 2D slab burner with a quartz visualization window allows obtaining multiple regression rate data in one single burn, as opposed to traditional regression rate measurement methods. The combustion chamber has a rectangular geometry, which requires the fuel grain to have this geometry in order to adapt to the quartz visualization window, as the experiments carried out in (Chandler, 2012), (Gouvêa, 2016) and (Nakagawa and Hikone, 2011). The configuration of the 2D slab is shown in Figure 4.

Figure 4. Configuration of the 2D slab burner

The oxidizer chosen for the current work was gaseous oxygen, which comes from a feed line system and is injected to the combustion chamber as it can be seen in Figure 5. The sensors and valves present in the feed line are a pressure regulator in the cylinder of oxygen, a solenoid valve that controls the opening and closure of the oxygen flow, a flow meter and check valve next to the combustion chamber. In case it is necessary to control the oxidizer flow during the test, a needle vale was added.
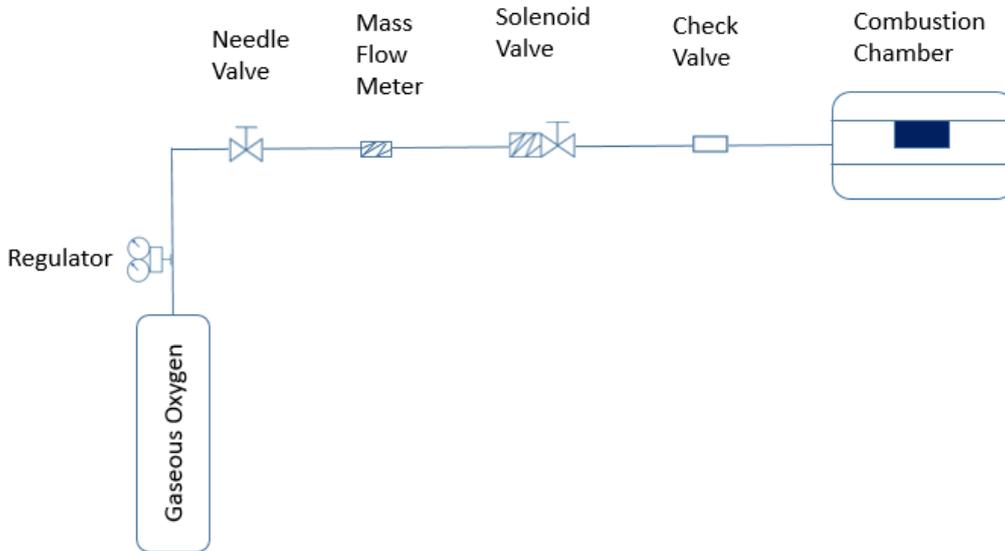
Figure 5. Feed line System.

2.3 Data Acquisition and Regression Rate Measurement

The regression rate ($\dot{r}$), or the rate at which the fuel burns can be obtained using several methos, the most used being the Eq. 1:

$$\dot{r} = aG_{ox}{}^{n} \tag{1}$$

where a and n are ballistic parameters, a being the pre-exponential factor and n the exponential factor. The parameters a and n can be obtained through the correlation of the experimental points with Eq. 1.

The data obtained is mainly visually through a camera positioned above the quartz window, with a capacity of 60 frames per second. The camera is the images were analyzed in an imaging software developed in MATLAB, considering intervals of 15 seconds due to the low fuel regression rate.

The instant regression rate obtained between two frames is shown in Equation 1, in which ΔH is the difference between the initial (H_i) and final height (H_f) of the grain, measured in millimeters, and Δt is the time interval, measured in seconds. In Figure 6, a schematic of the fuel grain in its initial configuration and a projection of a final height is shown in order to better understand the functioning of the visualization method.
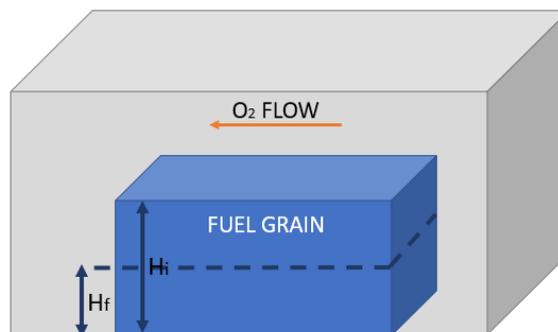
$$\dot{r} = \Delta H/\Delta t \tag{2}$$

Figure 6. Fuel grain positioned in its initial configuration and a projection of its final height.

3. RESULTS

The first attempt of burning was made with the fuel grain directly in touch with the quartz window, as performed by (Gouvêa, 2016). However, as it can be seen in Figure 7, the soot released hampered the visual methodology adopted for the work. Initially, the fuel grain contour can be clearly seen, but seconds after the start of the test, it was not possible to discern the limits, hence, the imaging analysis could not be performed.
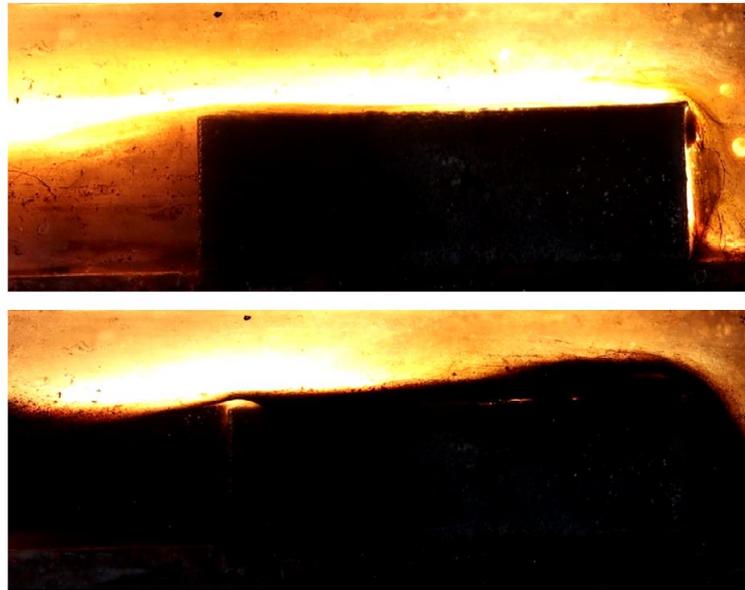

Figure 7. HTPB grain first test attempt.

As a second approach, it was left a small gap between the fuel grain and the quartz window. The soot released did not interfere in the analysis and it was possible to see a clearer boundary throughout the test time, as shown in Figure 8. Nevertheless, the light surface caused by the burn on the top face caused the image to burst in some frames. Filters and camera settings were implemented for further analysis, as well as modifications to the imaging software. With such modifications, it was possible to observe improvements in the analysis, however, it can be said that this filming methodology is not yet at the appropriate state. For future works, it is expected to use a thermal camera to better observe the boundaries of the fuel grain.

Figure 8. HTPB fuel grain image with further improvements in configuration and imaging modifications.

The results for regression rate, Figure 9, were obtained through the comparison of the two samples, HTPB fuel grain and HTPB with 3% of the CuAA catalyst. The HTPB curve in Figure 8, exhibits its lower regression rate. The results presented values accordingly to those found in the literature (George et al, 2001).
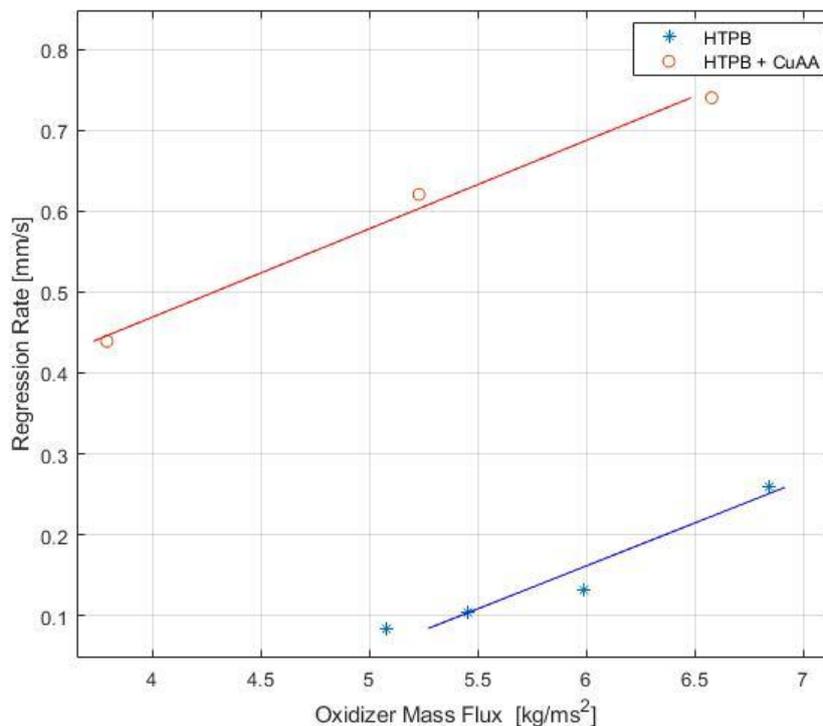
Figure 9. Comparison of the regression rate of the HTPB-based fuels grain samples with and without CuAA catalyst.

Comparing the regression rate curves of the HTPB-based solid fuel samples with and without the catalyst, it is possible to observe that the presence of the catalyst provided an increase of approximately 350% in the regression rate of the sample. According to (Cardoso et al., 2019), CuAA starts its decomposition at approximately 270°C, whereas in HTPB it starts at 430°C. The catalyst modifies the mechanism of decomposition of the polymeric fuel matrix, when initiating its decomposition (270° C), possibly acting as a free radical initiator in the degradation of the HTPB molecule by decreasing the energy barrier in the breaking of the urethane bond between HTPB and the curing agent IPDI (450°C). Thus, by forming intermediates, the presence of CuAA interferes in the final decomposition process of the HTPB-based solid fuel, increasing the availability of small vaporized molecules in the burning zone at higher rates and demanding lower temperatures.

4. CONCLUSIONS

This work evaluated the influence of the CuAA catalyst on the regression rate of HTPB-based fuel grains for hybrid rocket propulsion using a 2D slab burner. Preliminary experimental results point to an improvement of approximately 350% in the regression rate of the sample containing 3% of the CuAA catalyst in its formulation when compared to the sample without catalyst. The regression rate of the HTPB-based solid fuel sample matches values found in the literature for the chosen oxidizer mass flux range (GOX). It was necessary to make an adaptation to the methodology already developed in order to better visualize the borders of the fuel grain for further imaging software analysis and results treatment. For future work, other methodologies for better visual data acquisition should be adopted, for example a thermal camera.

5. ACKNOWLEDGEMENTS

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