Influence of Ammonia Borane on the Stability of a Liquid Rocket Combustor

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I. Introduction

The use of additives to tailor the combustion behavior of a system is a potential method of suppressing combustion instabilities in liquid rocket combustors. Traditionally, modifications to geometric features and operating conditions of a system have been used to influence combustion behavior and suppress combustion instabilities [1,2]. Such modifications are unique for each specific engine and propellant combination and are often determined by trial and error. A fundamental understanding of how additives could be used to promote stable combustion could presumably result in a more robust and generalized approach for producing stable engines.

Research has shown that additives can modify different aspects of the combustion behaviors of liquid fuels. Changes observed in experiments include lower ignition temperatures [3,4], reduced ignition delay [5], increased burning rate [6], and increased volumetric energy [7,8]. All these changes could possibly lead to a change in combustion dynamics and thus the stability of a system. Efforts were made by Kesselring and Oberg [2] to influence the stability of a combustor by adding aluminum and aluminum oxide to gelled fuels, and it was found that these additives produced more stable operation due to particle dampening. Pfeil et al. [10] added nanoaluminum to ethanol and JP-8 to determine the additives’ influence on stability and noted an increase in the combustion instability of the system when using ethanol but no change when JP-8 was the base fuel. Other efforts to use additives to influence the combustion stability of a liquid combustor are limited.

One potential additive is ammonia borane (AB), NH$_3$BH$_3$. At temperatures above 343 K, which is below the normal boiling point of ethanol (351 K), AB can dissociate into H$_2$ and BH$_3$. More H$_2$ is released at higher temperatures [11]. Experiments by Pfeil et al. [12] showed that the burning behavior of ethanol drops with AB differs from neat ethanol in two major ways. First, the droplet burning rate increased notably with the addition of AB, presumably as a result of hydrogen being added to the combustion process. The addition of hydrogen could also potentially prove advantageous in suppressing combustion instabilities as it has been shown to increase the flammability limits of a fuel [13–15]. Also, it is generally accepted that hydrogen-fueled rocket combustors tend to be less prone to combustion instability than their kerosene-fueled counterparts. Second, droplet scattering was observed later in the life of the droplet, leading to rapid fuel consumption and energy release, a behavior also seen with multicomponent droplets [16,17]. These differences resulted in two notably separate rates of energy release. As the addition of AB had a notable impact on the combustion behavior of droplets, a change in stability behavior might also be anticipated.

This paper describes an experiment that was conducted to compare the combustion dynamic behaviors between a neat liquid fuel and a fuel containing AB. A model rocket combustor with a well-documented behavior of self-excited instability using kerosene and gaseous methane fuels was used [18,19]. The main objective of this work was to determine if the changes in combustion behavior observed in droplet experiments would result in measurably different stability behavior in the model combustor. The different stability behavior could then possibly be related to the behaviors observed in the droplet combustion experiments. Experiments were performed in the model rocket combustor with neat ethanol and the ethanol–AB mixture. Stability characteristics in terms of pressure oscillation amplitudes as a function of combustor geometry and unsteady heat release profiles were determined for the two fuel types and compared.

II. Experimental Setup

A. Fuel Description and Preparation

The neat ethanol used in these experiments was obtained from Koptec, and the AB was obtained from Sigma Aldrich. The fuel was prepared by adding 6 wt % AB, the same concentration previously used by Pfeil et al. [12], to the ethanol and allowing the AB to dissolve completely, resulting in a solution. Experiments were performed within 12 h of mixing the fuel and at the conditions denoted in Table 1. This experimental fuel is not stable in the long term.

B. Experimental Configuration

The oxidizer used in this experiment was 90 wt % hydrogen peroxide and 10 wt % water. First, the oxidizer was passed through a catalyst bed gas generator, shown in Fig. 1. The hydrogen peroxide is decomposed into warm oxygen and water and then fed from an oxidizer manifold into a choked inlet that forms the upstream boundary of the combustor. One unique aspect of this experiment is the ability to translate the choked inlet during an experiment to change the combustor system resonance. The inlet tube resonance can be changed between a quarter-wave and a half-wave resonator.
with respect to the combustor acoustics. In addition to changing the system resonance, varying the resonance of the tube changes the flow dynamics in the tube and gives rise to different stability behavior as a function of tube length.

Once past the choked inlet, the oxidizer flowed through the oxidizer post and mixed with the fuel that was introduced to the system through a coaxial swirl configuration. A step expansion occurred immediately after the fuel injector as the fuel and oxidizer entered the combustion chamber. Ignition was achieved by introducing 50 ml of JP-8 into the combustion chamber before the experimental fuel arrived. JP-8 readily ignites with high-concentration decomposed hydrogen peroxide. The first third of the combustion chamber consisted of a quartz tube surrounded by an acrylic housing to provide structural support. This optical chamber allowed for visual measurements of the combustion process. The combustion products then traveled down the steel combustion chamber and out a short sonic nozzle.

Low-frequency (Druck PMP 1260 and PMP 1265 8-30 Vdc sampling at 500 Hz) pressure transducers were placed in various locations throughout the combustion system. High-frequency (Kulite WCT-312M sampling at 100 kHz) pressure transducers were located in the oxidizer and fuel manifolds, 7.6 and 0.6 cm upstream of the step expansion, and 36.8 cm downstream of the step expansion, 0.2 cm upstream from the nozzle. These pressure measurements allowed for analysis of mean pressures as well as high-frequency pressure variations. Further details of this setup can be found elsewhere [18, 19].

C. Measurement Techniques

Two high-speed cameras were used simultaneously for visualizing combustion light. The first system used a Vision Research Phantom sampling at 10 kHz and fitted with a Nikon 28-105 mm lens connected to a Thorlabs laser line filter with a 70% transmission (centered at 543.5 nm ±2 with a full width half maximum of 10 nm ±2). This filter was employed to bandpass light emitted by boron oxidation, as researchers have reported that boron compounds produce strong emission bands between 536 and 548 nm during combustion [20]. Water steam is also present in the combustor, which with oxygen can cause boron to react and form BHO2 [21]; however, BHO2 probably reacts with OH radicals producing BO2 [22], which has emission bands within the limits of the line filter. Thus, light emission obtained using this camera system should be a good indicator of the location of the boron reaction. The resulting images were partially obstructed by the combustor hardware, Fig. 2; thus, the image was smoothly interpolated across the obstructed part of the image using the Laplace equation before analysis of the data.

The other high-speed camera system employed a Video Scope International high-speed image intensifier (VS4-1845Hs) attached to another Vision Research Phantom sampling at 10 kHz. A Sigma 24-70 mm F2.8 lens with a Semrock interference filter (FF01-434/17-25) with a 90% transmission (centered at 434 nm with a full width half maximum of 21 nm) was attached to the camera assembly. The filter wavelength corresponds to the radical CH* that is present in early combustion reactions. This method has been used in previous efforts to evaluate the combustion response to pressure oscillations in an unsteady combustor [23].

III. Results

Operation of the combustor was the same for both fuels. Hydrogen peroxide begins to flow at time = 5 s into the experiment, Fig. 3. A nitrogen purge is activated in the fuel line at the same time so that no oxidizer will travel into the fuel lines, causing the pressure in the fuel manifold to rise to around 1500 kPa. The H2O2 reaches the catalyst bed, decomposes, and then begins to fill the combustor at time = 6 s. Once H2O2 decomposition and operation are well established, the fuel nitrogen purge is stopped and fuel begins to flow at time = 9 s. Ignition occurs around time = 10.4 s, causing a sharp rise in pressure in the fuel manifold and combustor. The oxidizer post position is kept constant for around 1 s to eliminate transient behavior caused by ignition and then begins to translate at time = 11.6 s. The post then translates at a rate of 5.1 cm/s for 2 s. Fuel flow is then terminated at time = 14.1 s, and the nitrogen purge in the fuel line is once again initiated. The H2O2 becomes depleted around time = 16.3 s, and the pressure within the combustor returns to its initial state. The resulting mixing of the fuel–oxidizer and combustion is close to complete for both fuels with characteristic
velocity efficiencies of 0.973 for neat ethanol and 0.959 for ethanol–AB.

Spectrograms were produced from the pressure measurement located 36.8 cm downstream of the injector face for both fuels and are shown in Fig. 4. These show the general spectral pressure response caused by combustion and variations in geometry. The spectrograms were generated after passing the pressure data through a high-pass filter at 200 Hz and then using a short-time Fourier transform with 4096 points and 50% overlap. The oxidizer post length is overlaid on the spectrogram to provide interpretation between geometry and frequency response.

The unsteady pressure response varies during operation of the combustor. Unsteady pressure oscillations are absent when H2O2 is flowing in the absence of fuel. For neat ethanol, the high-frequency instabilities are initially excited upon ignition but drop to a very weak response as the ignition spikes dissipate. The pressure response of the combustor remains this way even after translation of the oxidizer post begins. At time = 12.3 s, combustion becomes unstable, producing a strong pressure response with multiple harmonic frequencies that continues until time = 13.5 s. This unsteady combustion results in peak to peak pressure oscillations up to 1380 kPa, equivalent to 93% of the mean chamber pressure. For the ethanol–AB fuel, high-frequency instabilities are also excited upon ignition, resulting in peak to peak pressure oscillations up to 1240 kPa, equivalent to 84% of the mean chamber pressure; however, this pressure response remains consistent throughout operation of the combustor until time = 13.7 s.

Power spectral density (PSD) plots provide quantitative values of the magnitude of the spectral content of the unsteady pressure oscillations, Fig. 5. The PSD plots are produced using the same pressure measurement 36.8 cm downstream of the injector face while using a 0.1 s time slice and 16,384 points in a fast Fourier transform. Four different times were selected in order to provide information about the stability of the combustor before ignition: time = 10 s; after ignition and before translation of the oxidizer post, time = 11 s; and for two different times during translation, time = 12 and 13 s.

While only decomposed H2O2 is flowing through the combustor, no coherent frequency content is observed, as expected, Fig. 5a. After ignition, Fig. 5b, the experiment using neat ethanol begins to experience weak pressure oscillations, and the first, second, and fifth longitudinal modes become distinguishable. The experiment using the ethanol–AB fuel experiences strong pressure oscillations producing distinguishable frequency content in the first seven longitudinal modes with the first mode having the highest strength. As the oxidizer post begins to translate, Fig. 5c, the experiment with neat ethanol continues to have similar weak pressure oscillations and similar frequency content in the longitudinal modes; however, the content in the second mode does increase, producing similar strength as the first mode. As the oxidizer post translates even further, the experiment using neat ethanol eventually experiences strong pressure oscillations that produce frequency content in the first seven longitudinal modes of the combustor with the majority of the strength in the first mode. For the experiment using the ethanol–AB fuel, translation of the oxidizer post results in similar strong pressure oscillations with more strength in the first longitudinal mode and less strength in the higher modes.

The effects of adding AB on the stability of the first acoustic mode of the system can be seen in Fig. 6. As discussed earlier, the oxidizer post length changes during the experiment. Figure 6a shows the peak value of the first mode for various oxidizer post lengths taken from the PSD analysis, discussed in Fig. 5, whereas Fig. 6b shows the corresponding frequency. Both fuel types produce unstable combustion behavior for oxidizer post lengths between 10.1 and 16.6 cm at nearly the same magnitude; however, the fuel containing AB exhibits unstable combustion behavior for both longer and shorter oxidizer post lengths than the neat ethanol fuel. The frequency of the first acoustic mode also has a measurable increase with the addition of AB.

The addition of AB also influences the location of unsteady heat release within the combustor, as shown in Fig. 7, which shows the location of unsteady heat release for selected oxidizer post lengths spanning the range of geometries. The data used to produce the plots in Fig. 7 were obtained by applying a PSD analysis to the optically filtered emission fluctuations from 39 sections, 1.27 cm tall by 0.32 cm wide, corresponding to the centerline of the optical chamber. The PSD analysis used a 50 ms time slice and 512 points in a fast Fourier transform. Peaks at the frequency of the strongest first longitudinal (1L) mode were obtained and then plotted as a function of distance from the injector. The data were then normalized by the maximum peak from all the geometries tested for each fuel. Unsteady heat addition is not shown for the neat ethanol case at oxidizer post length = 19.1, 17.8, and 10.2 cm because those cases were stable.

Ethanol combustion shows a peak in CH* emission occurring about 5 cm downstream of the injector face, whereas the CH* and boron oxidation emissions for the ethanol–AB fuel have a bimodal distribution, with maxima near the injector and toward the aft end of the optical section. Furthermore, the magnitude of unsteady boron oxidation near the aft end of the chamber is consistently higher than it is near the injector. The droplet experiments indicated that boron oxidation occurred after ethanol combustion [12], which is consistent with more boron oxidation fluctuations occurring later in the chamber.

The final significant change to note is the effect of the additive on the temporal unsteady heat release. Of particular interest is the temporal relationship between local pressure and heat release, because a positive correlation will lead to amplification of the
pressure oscillation according to Rayleigh's criterion and because pressure provides a useful reference in the stationary system. It is also likely that the dominant coupling mechanism can be linked to the stationary fluid dynamics that can be defined by the easily measurable pressure modes. However, because the pressure mode comprises both upstream and downstream traveling waves, the exact role that each play in the initiation and sustenance of the combustion instability is not clear.

The temporal relationship between pressure and light emission oscillations is defined here as the phase angle. To determine the phase angle, the time between two separate peaks in the pressure oscillations, Fig. 8a, is averaged for 50 ms of oscillations for a particular geometry and then set equivalent to 360 deg. The time between the peak light emission and pressure oscillation is then determined, Fig. 8a, averaged for 50 ms of oscillations, and then converted into a phase angle using the average time between peak

Fig. 5 PSD of neat ethanol (left column) and ethanol with 6 wt % AB (right column) for times of a) 10 s, b) 11 s, c) 12 s, and d) 13 s into operation of the combustor. Measurement was made 36.8 cm downstream of the injector face.
pressures. The light emission waves are determined by averaging the light emission over 39 sections, 1.27 cm tall by 0.32 cm wide, corresponding to the centerline of the optical chamber. The pressure in the clear combustion chamber was inferred from the pressure measurement obtained 36.8 cm downstream of the injector face, Fig. 8b. This was done by finding the theoretical speed of sound of the combustion products using the NASA Chemical Equilibrium with Applications (CEA) thermochemical code [24] and using this value to determine the convective speed of the flow within the combustor assuming a constant speed of sound. Knowing the speed of sound and the convective speed of the flow allowed for determining the location of the pressure wave throughout the combustion chamber.

The plots in Fig. 9 show the relative phase angle of the local maximum of the unsteady flame emission signal with respect to the local maximum of pressure. Because the injector face is a reflecting surface, both upstream-running (reflected from the throat) and downstream-running waves are present. In Fig. 9, a positive phase angle indicates the peak in light emission leads the peak in pressure; hence, the phase angle of the downstream-running wave with respect to light emission is always more positive than the phase angle of the upstream-running wave. A phase angle within ±90 deg indicates an amplification of the compression wave according to the Rayleigh Criterion. Under most cases, the phase angle plots indicate that the unsteady energy release can couple with either type of wave.

Neat ethanol exhibits phase angles that are fairly linear with respect to the location within the combustor for each oxidizer post length; as might be expected, a main difference between the correlations with upstream and downstream traveling wave phase angles is whether the slope with respect to location is negative or positive. The addition of AB to the fuel results in more complicated behavior for each oxidizer post length. The phase angle in the front end of the optical section exhibits a linear trend, whereas the phase angle in the aft part of the optical section is still sufficiently in phase with the upstream traveling compression wave as the unsteady heat release toward the aft end of the quartz chamber is still sufficiently in phase with the upstream traveling compression wave to produce an amplification of the pressure response. Neat ethanol does not demonstrate unsteady behavior for these oxidizer post lengths because most of the unsteady heat release occurs around 5 cm downstream of the injector, which is out of phase with the pressure oscillations.

For the longer oxidizer post lengths between 16.6 and 19.1 cm, the system is again stable for neat ethanol and unstable for ethanol–AB. This is a surprising result, as it would appear that the unsteady heat release for neat ethanol at 5 cm downstream of the injector would be in phase with the pressure oscillations, resulting in unsteady combustion. A possible explanation for this behavior arises again from the differences in the combustion dynamics of the two fuels. The ethanol–AB fuel appears to partially react near the injector and then complete the reaction near the aft end of the quartz chamber on the following unsteady combustion cycle. The partial reaction of the fuel allows the remaining fuel to preheat and mix more uniformly with the oxidizer, possibly making the premixed preheated reactants more susceptible to disturbances toward the aft end of the chamber. This bimodal combustion behavior is absent for neat ethanol combustion.

IV. Conclusions

An unstable model rocket combustor was tested with neat ethanol and with ethanol containing AB. Different behaviors were noted. The combustor tested with ethanol–AB was unstable over a wider range of geometric configurations, and the unsteady heat release profile, as indicated by flame emission from CH* and oxidized boron, was different between the two cases.

With the addition of AB, the unsteady heat addition is characterized by a bimodal distribution of unsteady heat release as indicated by optically filtered flame emission. Both the spatial and temporal distributions were affected. The system is unstable for the ethanol–AB fuel for oxidizer post lengths between 9.1 and 10.1 cm, as the unsteady heat release toward the aft end of the quartz chamber is still sufficiently in phase with the upstream traveling compression wave to produce an amplification of the pressure response. Neat ethanol does not demonstrate unsteady behavior for these oxidizer post lengths because most of the unsteady heat release occurs around 5 cm downstream of the injector, which is out of phase with the pressure oscillations.

For the longer oxidizer post lengths between 16.6 and 19.1 cm, the system is again stable for neat ethanol and unstable for ethanol–AB. This is a surprising result, as it would appear that the unsteady heat release for neat ethanol at 5 cm downstream of the injector would be in phase with the pressure oscillations, resulting in unsteady combustion. A possible explanation for this behavior arises again from the differences in the combustion dynamics of the two fuels. The ethanol–AB fuel appears to partially react near the injector and then complete the reaction near the aft end of the quartz chamber on the following unsteady combustion cycle. The partial reaction of the fuel allows the remaining fuel to preheat and mix more uniformly with the oxidizer, possibly making the premixed preheated reactants more susceptible to disturbances toward the aft end of the chamber. This bimodal combustion behavior is absent for neat ethanol combustion.

Both fuels show similar magnitudes in instability for the middle oxidizer post lengths because all the unsteady heat release for both fuels is occurring sufficiently in phase with the acoustics of the system to drive the unstable behavior. Theoretical calculations performed using the NASA CEA thermochemical code [24] indicate a temperature decrease of only a few degrees Kelvin with the addition of 6 wt % AB to the fuel; thus, we should not observe an increase in the magnitude of the instability with the addition of AB to the fuel based on that alone. The addition of AB also negligibly decreases the sonic velocity within the combustion chamber, which would result in similar instability frequencies for both fuels; however, the frequency increases with the addition of AB. The increase may result from the modified bimodal spatial unsteady heat release producing more
regions of elevated temperatures, allowing the pressure oscillations to travel faster in the chamber.

From both the droplet experiments and the combustor experiments, it appears that there may be two distinct phases of energy release. Ethanol appears to react first, leaving a mixture of ethanol and AB decomposition products, including boron, to react later. The result in this experiment seems to be another opportunity for the acoustic and the unsteady heat release modes to be in phase. It could be speculated that additives should be implemented in liquid combustors that result in a uniform energy release. Of course, it is also

![Graphs showing normalized peak of 1st mode](image)

Fig. 7 Relative amplitudes from emissions of CH* and boron for selected oxidizer post lengths as a function of distance from the injector face. Amplitudes are taken from a PSD analysis of the emission signal at a frequency corresponding to the 1L mode of the chamber. Peaks are normalized by the highest peak of all of the oxidizer post lengths investigated, data are taken from the centerline of the combustion chamber, and data are only displayed for fuels that exhibited unstable combustion at that oxidizer post length except for Fig. 7g, for which all fuels exhibited steady combustion. Oxidizer post lengths (OPLs): a) 19.1 cm, b) 17.8 cm, c) 16.5 cm, d) 14.0 cm, e) 11.4 cm, f) 10.2 cm, and g) 8.9 cm.
Fig. 8  Schematics depicting how phase angles were determined: a) schematic of the relationship between peak light emission and maximum of traveling pressure waves and b) schematic of correlating pressure measurement at the aft end of the combustor to pressure throughout the combustor.

Fig. 9  Temporal phase angle of local maximum in light oscillations with respect to local maximum in unsteady pressure oscillations. Data are only displayed for fuels that exhibited unstable combustion at that oxidizer post length. OPL: a) 19.1 cm, b) 17.8 cm, c) 16.5 cm, d) 14.0 cm, e) 11.4 cm, and f) 10.2 cm. The vertical lines indicate the location of the highest light emission fluctuations from Fig. 7 and are added for reference.
possible that this bimodal energy distribution could be stabilizing, if the injector design can temporally decouple unsteady combustion from the chamber pressure modes.

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References


Fig. 10 One cycle of neat ethanol, CH* filter (left column); ethanol with 6 wt % AB, CH* filter (center column); and ethanol with 6 wt % AB, green filter (right column). Measurements were for an oxidizer post length of 16.5 cm. Time steps between each image are the same. False coloring is added to the images to accentuate magnitude of heat release.


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Associate Editor