Effects of ammonia borane on the combustion of an ethanol droplet at atmospheric pressure

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ABSTRACT

Adding compounds rich in hydrogen to liquid fuels has the potential to change combustion behavior and enhance performance. One potential additive is ammonia borane (AB), which contains 19.6 wt.% hydrogen and can be dissolved in anhydrous ethanol (up to 6.5 wt.%). The particular system studied here would have limited use due to energy density and stability but is studied as a model system. Single droplet combustion experiments were performed with AB concentrations in ethanol varying from 0 to 6 wt.%. Measurements performed using high speed (5 kHz) planar laser-induced fluorescence (PLIF) indicate that hydrogen gas addition from the decomposition of AB continues throughout the droplet burning process. The hydrogen addition leads to an increase in the D^2 law rate constant, k_0, of up to 16%. While AB (and residual material) participates throughout the combustion process, it dramatically impacts the combustion behavior at the end of the droplet lifetime as the concentration of AB residual grows within the droplet. This results in droplet shattering, causing fine atomization and rapid combustion of the remaining fuel. Boron is also oxidized in this short period of time, increasing the energy released. In combustors, droplet shattering could enhance mixing and increase combustion efficiency. Thus, the approach of adding compounds rich in hydrogen is a promising method to introduce H_2 gas to practical combustion systems, while enhancing performance.

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1. Introduction

Recently, several efforts have been made to alter the combustion behavior of fuels by adding hydrogen (H_2) gas to combustion systems [1–3]. Guo et al. [4] reduced combustor pollutant emission levels while increasing the combustion efficiency of a fuel through the addition of H_2. Hydrogen has also lowered the flammability limits of fuels, allowing combustors to operate fuel lean; this in turn has promoted lower pollutant emissions [5–7]. Gaseous hydrogen has shown potential in stabilizing a normally unstable rocket combustor [1] suggesting that hydrogen addition to other fuels could produce similar effects. It has been shown by Rosen et al. [2] that as little as 5 wt.% addition of gaseous hydrogen to gaseous methane could change the stability characteristics of a system by influencing the combustion dynamics.

The current method of introducing H_2 into a combustor is to inject it into the fuel line or combustor from a separate storage tank. While acceptable for research purposes, this method is impractical for many applications due to the large volumes required to store gaseous H_2, or the challenging cryogenic requirements of using liquid H_2. One possible solution that has remained relatively unexplored is to introduce H_2 into the fuel through additives with high hydrogen content such as metal hydrides, boranes, or other molecules chosen for use as additives. In addition to potentially being a more practical pathway of introducing H_2, high hydrogen additives also have the potential of increasing energy density and overall fuel performance.

However, when evaluating an additive and its potential effects on the combustion process of a system, determining when and how hydrogen is released from the fuel into the system becomes important. This is because the combination of different liquid fuels and additives will result in varied hydrogen generation rates, which in turn will result in varied combustion dynamics. For example, combining high boiling point liquid fuels and additives with low decomposition temperatures will likely introduce hydrogen into the combustion process early and may allow it to influence the combustion behavior of the system. Alternatively, combining low boiling point liquid fuels and additives with high decomposition temperatures may tend to have the opposite effect, releasing hydrogen late, essentially inhibiting the influence of hydrogen in the combustion process and possibly rendering the additive ineffective. In addition, many additives can leave a residue

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that is also combustible. When and how this residue reacts is also important.

The objective of this work is to evaluate ammonia borane (AB) as an additive to ethanol fuel as a convenient model system. These two components were selected due to the high concentration of hydrogen (19.6 wt.%) in AB and the close proximity of its decomposition temperature to the boiling point of ethanol. Investigation on how AB addition influences the combustion process of the combined fuel is presented in this work. These questions are investigated through a series of fundamental, single droplet experiments performed using high speed cinematography and high speed OH planar laser induced florescence measurements. These experiments provide insight into combustion behavior and allow for dynamic observations of the effect of AB addition on the combustion of ethanol.

2. Experimental setup

2.1. Fuel

The two types of AB used for these experiments included AB from Sigma Aldrich, 97% pure, and AB produced at Purdue University through a process developed by Ramachandran and Gagare [8], 98% pure. Loadings of 3 and 6 wt.% of AB dissolved into ethanol were investigated. The AB was dissolved into 200 proof ethanol manufactured by Koptec. The resulting fuel mixture appeared unstable and slowly evolved gas over a period of several months. Because of this, the fuels were used within a few days of preparation.

2.2. Droplet combustion

Droplets were suspended on fine quartz rods with beads formed at the end, a method previously used by other researchers [9,10]. Quartz was chosen due to its relatively low thermal conductivity, which results in minimal heat transfer to the droplet. Quartz rod diameters directly above the bead ranged from 62–192 μm. Bead sizes ranged from 217–376 μm. Several droplets of neat ethanol were burned on each rod before burning a droplet containing AB. The rods were cleaned between droplet burns using a butane flame. After the combustion of two droplets containing AB, the rod was changed to avoid possible effects of buildup of AB combustion products.

The quartz rods were suspended in a clear, open top acrylic box with an aluminum bottom to minimize convective effects on droplet combustion. A coiled 30 gauge Nichrome wire was inserted through the side of the acrylic box and positioned near the droplet. A voltage was applied across the wire causing it to heat and ignite the droplet. After ignition, the Nichrome wire was quickly removed to avoid interaction with the combustion process. Backlighting by a halogen lamp placed behind an Interfit translucent light reflector provided a contrasting, white background. A Vision Research Phantom V. 7.3 black and white high speed camera was operated at a frame rate of 5000 fps, a pixel resolution of 320 × 240, and a 14 bit image depth. A schematic diagram of this experimental system is shown in Fig. 1. The videos taken using the high speed camera were analyzed using MATLAB software [11] to determine the equivalent diameter of the measured droplet cross-sectional area as a function of time.

The high speed camera was used with two lens configurations. The first configuration consisted of an Infinity Photo-Optical Company K2 Long Distance Microscope lens and was used to make general observations of the combustion behavior. The second configuration consisted of a Thorlabs laser line filter with the Infinity K2 lens. The filter had a transmission of 70%, a center wave-
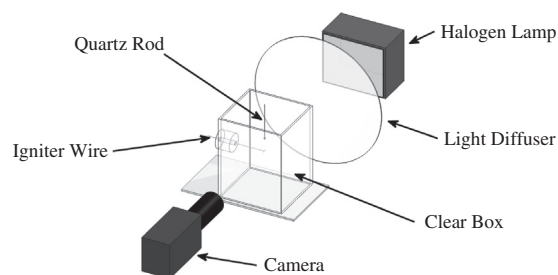

Fig. 1. Schematic diagram of the droplet combustion experiment.

length of 543.5 nm ± 2, and a full width half max of 10 nm ± 2. This filter was selected to isolate bands of emission from the oxidation of either boron or boron compounds which emit between 536 and 548 nm [12]. This method allowed for a qualitative indication of where and when boron combustion was occurring. A Vision Research Phantom V. 7.3 color high speed camera, with the same Infinity K2 lens, was also used without backlighting to record general combustion behavior, primarily to observe the flame during combustion.

2.3. High Speed Planar Laser-Induced Fluorescence (PLIF) system

A brief description of the high speed PLIF system is given here. For further details about the system, the reader is referred to Hedman et al. [13]. A Sirah Credo (CREDO-DYE) dye laser was pumped at a repetition rate of 5 kHz by an Edgewave Nd:YAG (IS811-DZ) solid state laser. The pulse energy of the frequency-doubled 283.23 nm beam from the dye laser was measured to be 0.15 mJ/pulse.

The beam was expanded vertically and horizontally using a negative spherical lens ($f = -75$ mm, Clear Aperture (C.A) = 21.3 mm) and expanded further horizontally using another negative cylinder lens ($f = 50$ mm, C.A = 21.3 mm). The beam was then focused using a positive spherical lens ($f = 500$ mm, C.A = 50.0 mm) resulting in a well collimated beam having a large circular cross section of approximately 5 cm. A thin sheet was then produced after the light was focused through a square cylindrical lens ($f = 250$ mm, C.A = 43.2 mm $*$ 43.2 mm). The distance between these lenses was adjusted to change the sheet height and width. The width of the beam was much smaller than the droplet initial diameter and was tall enough to capture the diffusion flame around the droplet.

The laser wavelength was set to 283.2 nm to excite the Q1(7) OH line. Experiments were also performed at a laser wavelength of 283.1 nm that did not excite the OH radical, thus allowing us to distinguish between broadband fluorescence and the OH radical. Experiments performed using the wavelength of 283.1 nm will be referred to as "detuned."

The fluorescence signal was recorded using a UV intensifier, high speed camera assembly. A Video Scope International high speed image intensifier (VS4-1845HS), capable of operating at 100 kHz with a gain of up to 80,000, was attached to the Vision Research Phantom V. 7.3 camera. A UV-grade lens (UKA Optics – UV1054B 105 mm F/4.0 Quartz Lens) was attached to the UV intensifier. A Semrock interference filter (FF01-320/40-25) with a transmission of 74% at 310 nm was used to transmit OH fluorescence and block broadband flame emission and scattered laser light. This camera assembly was placed perpendicular to the laser plane as shown in the schematic diagram in Fig. 2.

Acquired images were processed with MATLAB software [11]. Droplet diameter and OH intensity distributions were recorded. The laser caused the droplet itself to fluoresce, thus allowing the droplet diameter to be determined from this fluorescence. The