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ORIGINAL ARTICLE

Radiation-induced pyrolysis of solid fuels for ramjet application

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Abstract A wide variety of hydroxyl-terminated polybutadiene (HTPB) based fuels are experimentally assessed in anaerobic reaction. In this study HTPB pyrolysis is investigated using a CO_2 laser as the energy source. The formulation of the solid fuel samples is systematically changed to isolate the effects of carbon black, metal fuel additives, and small amounts of oxidizer. In addition, chemical changes to the fuels including curative type and base polymer are varied. Rates of pyrolysis reaction are reported for a wide range of solid fuels applicable to ramjet application. Processes involving the sintering together of metal particles, accumulation of carbon black, and formation of a melt layer are found to affect the reaction rate. It is determined that the surface composition is the most influential factor influencing the regression rate of HTPB based fuels.

1. Introduction

The solid fuel ramjet (SFRJ) continues to be an attractive propulsion system because it offers a good balance of simplicity, specific impulse, speed, and safety [1]. Research on the SFRJ gaseous oxidizer-solid fuel combustion environment has been conducted for decades and continues to be active today. Netzer et al. [2,3] led an effort to build a small scale SFRJ combustor for the development of predictive numerical tools [4]. Similar studies over the years have utilized sub-scale burners to investigate the flame stability [5,6], inlet design [7], and development of high fidelity fluid dynamic numerical tools [8,9].

Sub-scale SFRJ motors have also been used to investigate high density fuel formulations comprised of polymer with imbedded metal particles [10,11]. The most commonly used fuel is hydroxyl-terminated polybutadiene (HTPB).

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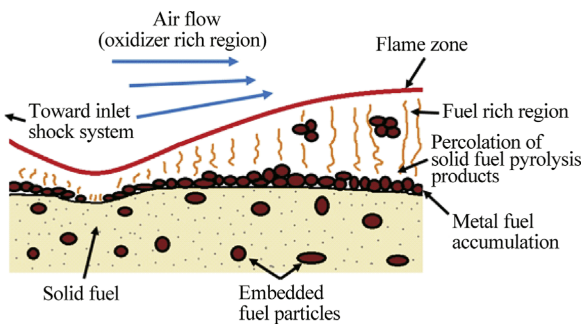

Figure 1 A depiction of the combustion environment of a solid fuel ramjet (SFRJ). Due to boundary layer formation, much of the regression of the fuel grain is driven by pyrolysis. A diffusion flame forms between the oxidizer flow and the pyrolysis products.

This polymer is important to the propulsion community due to widespread application in rocket motors, hybrid systems, and solid ramjet applications. The prevalent use of HTPB is a result of desirable mechanical properties at a wide range of temperatures, even when highly loaded with particles. These advantages are described in greater detail elsewhere [12,13]. For an HTPB based fuel with metal additives, the combustion environment in a typical SFRJ is depicted in Figure 1. Here a solid fuel is shown with embedded metal particles added to increase density and energy content. The blue lines above the fuel grain represent the high velocity cross-flow of the oxidizer stream. This flow rapidly forms a boundary layer above the fuel surface, immediately following expansion near the inlet shock system [14]. Since oxidizer penetration of this boundary layer is limited by the flow characteristics, radiation from the flame zone (red) accounts for much of the heat transfer back to the fuel surface. The pyrolysis products diffuse toward the flame zone, often percolating through accumulated metal particles at the surface. The formation of a boundary layer and a diffusion flame with a standoff distance results in an increased importance on the radiative heating of the fuel surface and the resulting pyrolysis [15]. Condensed phase conduction also becomes increasingly important since surface has higher thermal conductivity due to the accumulated metal. The absorption and dispersion of heat through the solid fuel is complex because radiation, conduction, and convection all significantly contribute.

Both the widespread use of HTPB in various propulsion systems and the vital role of pyrolysis have motivated many studies on the subject. Many of these studies have been reviewed by Beck [16]. In short, various techniques have been used to rapidly heat fuel samples to measure their decomposition [17] and pyrolysis rates [18,19]. This information is typically used to determine chemical kinetic parameters or reaction mechanisms [20,21]. Esker and Brewster [22] carried out experiments to quantify the pyrolysis rate of IPDI cured HTPB. A CO_2 laser was used as the heat source and anaerobic regression rates were determined using a micro-force transducer for heat fluxes between 50 and 500 W/cm^2. It was found that 3 wt% carbon black decreases in the pyrolysis rate of up to 50%. Pyrolysis rates have been reported previously for HTPB, however, typically this is done for a single fuel and attention is focused on the technique rather than systematic changes to the fuel.

The current study seeks to expand previous HTPB pyrolysis studies by examining the effect of various additives, curative, and changes to the polymer. This is motivated by the fact that isolated HTPB pyrolysis studies often cannot be compared due to chemical differences in the fuel and by a lack of data regarding the effect of additives on pyrolysis rate. The goal of this study is to determine the effect of the curative, polymer, added carbon black, and metal fuel additives on the pyrolysis rate and surface behavior.

2. Experimental methods

2.1. Fuel preparation

The solid fuels prepared in this study are all HTPB based, systematically modified to study the effects of curative type, polymer type, carbon black, metal fuels, and oxidizer. In most of the fuel formulations, the HTPB used is an R45-M (604045, RCS RMC) cured with: isophorone diisocyanate (IPDI, Sigma Aldrich MFCD00064956) or a polymethylene polyphenylisocyanate (PAPI 94, Dow Chemical 94 MDI). For those formulations containing a large amount of micron-sized additives, the PAPI 94 curative was used as the cure times are very short compared with IPDI, typically about 20 minutes in the ratio used. The advantage of the short cure time is that the colloidal mixture becomes tacky and increasingly viscous quickly, severely limiting settling of added particles.

Additives to the polymer based fuels were carbon black (Cancarb N991), aluminum (Valimet, H-3), boron (Mach I, Boron 95), a magnesium boron mixture (Mach I, 60 wt% Mg), and ammonium perchlorate (AP, Sigma Aldrich 208507). The particle sizes for these additives are listed in Table 1 along with formulations for each fuel. For details regarding specific ingredients, the reader is directed to the manufacturer, as each ingredient is commercially available. In the preparation of each sample, the HTPB was degassed under vacuum for 15 min prior to mixing. Ingredients were added and mixed by hand following more exposure to vacuum to release air voids and evolved gas bubbles from the mixture. Teflon containers of the fuels were cured in an oven at 65 °C.

Three different polymers were used in the fuel formulations: HTPB R45M, HTPB HTLO (R-45HTLO, Cray Valley), and Krasol® (HLBH P-3000, Cray Valley). Both HTPB R45M and HTLO have a molecular weight near 2800 g/mol and differ only by the higher polydispersity of HTLO. A higher molecular weight of 3100 g/mol is reported for HTPB Krasol®, a fully hydrogenated hydroxyl-terminated polyolefin. Details regarding the physical and chemical properties of these polymers can be found in Ref. [23]. All measurements reported for each formulation were made using samples from the same mix and cast.