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Pyrolysis-gas chromatography mass spectroscopy and pipe combustor analysis of the ignition and mass regression characteristics of a sulfur doped polysulfide ramjet fuel

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ABSTRACT

The autoignition and low pressure combustion characteristics of five candidate polysulfide (LP-33) based ramjet solid fuel formulations are evaluated using pyrolysis-gas chromatography mass spectroscopy and a subscale pipe combustor. The polysulfide based fuels are oxidatively cured using p-quinone dioxime and manganese dioxide. The fuel formulations differ by the amount of elemental sulfur that is added to alter the decomposition temperature, mass burning rate, and to modify the mass fraction of low ignition temperature sulfur based decomposition gasses. The objectives of this research are to demonstrate that the autoignition temperature and the mass regression rate of the candidate fuels can be tailored as function of the sulfur doping fraction. The results of the analysis show that the mass fraction of low autoignition temperature decomposition gasses that include carbon disulfide and hydrogen disulfide increase as the mass fraction of elemental sulfur increases in the fuel formulation. Pipe combustor test results demonstrate repeatable autoignition temperatures less than 400 °C at ambient pressure for all formulations. The results also show that the primary effect of sulfur doping is to lower the mass burning rate of the fuel in direct correlation to the Shore-A hardness of the material which increases the time to ignition with no appreciable change to the mean autoignition temperature.

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1. Introduction

The impulse-density performance advantage of solid fuel ramjets (SFRJ) over conventional solid propellant rocket motors is well established both analytically and experimentally. The superior volumetric loading efficiency of available energy in the SFRJ is easily understood by the recognition that all oxidizer in a conventional solid propellant rocket motor is replaced by fuel as all oxidizer in the SFRJ is derived from free stream air. This great advantage also presents several widely accepted engineering challenges in the design of a SFRJ, particularly in the fuel formulation, if the full performance advantages are to be realized. High altitude flight where positive thrust to drag ratios can be achieved at low fuel flow rates requires fuels to have stable combustion at low equivalence ratios (ER) nearing the lower fuel flammability limits. The advantage of fuel formulations with low decomposition and autoignition temperatures is well appreciated in the ramjet design community. As the fuel decomposition temperature increases, boost velocities must increase or secondary ignitions sources are required. Additionally, fuel with high decomposition temperatures require greater heat feedback from the combustion zone to retain the flame and may not reignite should flameout occur. Each of these design challenges suggests that a fuel formulation with low decomposition and autoignition temperatures and expanded flammability limits is advantageous for the SFRJ.

The relationship between the air to fuel ratio (AF), or equivalence ratio (ER), and the impulse-density is shown in Fig. 1. The impulse-density of the fuel–air mixture increases proportionally to a peak value as the AF ratio increases as is demonstrated in Eq. (1). Eq. (1) is a simple manipulation of the momentum equation for a ramjet showing the ideal impulse-density as a function of the AF ratio, the gross I_{sp}, and the freestream momentum loss where U_∞ is the freestream velocity. Figure 1 plots Eq. (1) for three LP-33 polysulfide (PS) ramjet fuel formulations operating at a freestream Mach number and altitude of 3 and 18.2 km respectively. The stoichiometric AF for these formulations is approximately 7.3. Note that the impulse-density increases as the ER decreases down to approximately 0.5 with a gradual decline as the ER continues to drop. For the selected materials in the plot, the peak impulse-density occurs at an AF ratio between 12:1 and 15:1 which is approximately twice the stoichiometric AF ratio. The figure illustrates that peak SFRJ performance dictates efficient combustor operation at ER well

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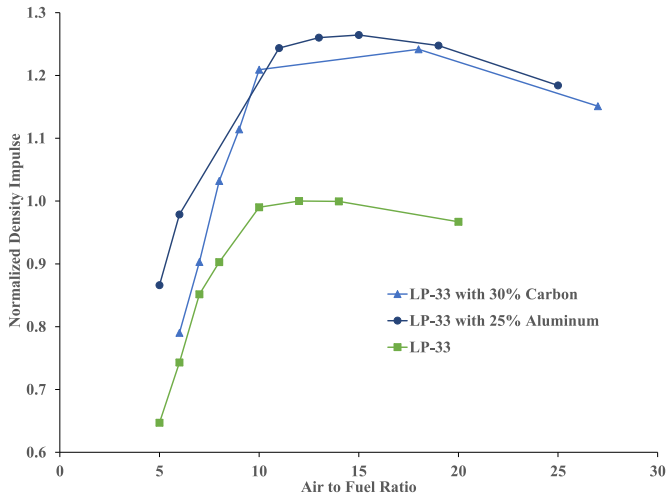

Fig. 1. Theoretical impulse density versus AF ratio and ER for vireos ramjet fuels.

off of stoichiometric,

$$\text{Impulse density} = (\text{AF}+1)I_{\text{SP}_{\text{gross}}} - \frac{\text{AF}\,U_\infty}{g}. \quad (1)$$

Elemental sulfur has been widely used in the vulcanization of rubber for many years having been shown to alter the material toughness and thermal stability [1]. Sulfur has also been used as a curing agent in composite solid rocket propellants with LP-33 binders since the 1950s [2]. McDonald et al. investigated the decomposition characteristics of oxidatively cured fuel samples of LP-33 as a function of the doping fraction of elemental sulfur [3]. Their DSC and TGA analysis showed that the temperature for the onset of decomposition of the LP-33 based fuel can be reduced from 283 to 237 °C as the doping fraction moves from 0% up to 6.8%. The use of elemental sulfur as an ignition aide in pyrotechnics and black powder systems has a significance historical precedence [4]. The 8-member sulfur ring begins to fragment at 140 °C and has a demonstrated autoignition temperature in air of 232 °C [5,6]. Additionally, sulfur cured systems decompose into gasses with low autoignition temperatures to include hydrogen sulfide and carbon disulfide, both having autoignition temperatures below 250 °C [7,8]. These demonstrated characteristics of elemental sulfur form the bases for using sulfur as a dopant in the present research.

SFRJ ignition has been investigated by several researchers to include autoignition by laser and hot gas streams [9–17]. Of particular interest is the work performed by Kashiwagi et al. [11–13,16] where the ignition of polymer samples was examined in an oxidizing hot gas stream. A general summary of their conclusions was that gas phase ignition mechanisms dominated over solid phase. Several numerical models have been developed for the investigation of polymer ignition [18–21]. Tahsini's [21] work concluded that the ignition delay time was directly related to the evaporation delay time with a weak dependency on inlet velocity and a strong dependency on inlet air temperature. Other relevant work has included pyrolysis, with and without mass spectroscopy which has been used to study the regression rate of fuels and the constituents of the decomposition gasses evolved from the polymer surface [22,23]. Sundarrajan et al. [24] used pyrolysis mass spectroscopy and flash pyrolysis gas chromatography to investigate the thermal degradation of two polysulfide copolymers. Finally, Hedman [25] extensively used a CO_2 laser in non-oxidizing pyrolysis of several HTPB based ramjet fuels primarily to assess regression rate dependency on fuel additives and curative types. His work has concluded that the fuel surface composition has the highest influence on the regression rate of the HTPB based fuels.

Presented in this paper are pipe combustor and pyrolysis gas chromatography mass spectroscopy results for five PS ramjet fuel formulations with elemental sulfur doping weight fractions ranging from 0 to 6.8%. This investigation is a continuation of previously reported experiments that showed by TGA and DSC analysis that the fuel decomposition temperature for the identical PS formulations can be manipulated by the sulfur doping fraction, all of which was shown to be less than 313 °C [3]. The primary objective of this work is to demonstrate the manipulation of the autoignition temperature and mass burning rates for the fuel formulations as a direct result of the sulfur doping fraction. The work demonstrates through pyrolysis gas chromatography mass spectroscopy that the partial pressures of low ignition temperature, gas phase fuel thermal decomposition products, which include hydrogen disulfide and carbon disulfide, can be altered by the fuel's elemental sulfur doping weight fraction. Pipe combustor analysis is used to assess the autoignition temperatures, mass burning rate and combustion efficiency of the formulations subject to a low velocity oxidizing cross-flow stream of ambient pressure air.

2. Experimental procedure and material properties

2.1. Ramjet fuel formulations

Table 1 shows the variations on five LP-33 based fuel formulations that are considered in this investigation [26]. The table shows the mass fraction of sulfur, the sulfur to accelerant ratio, the measured Shore-A hardness, and the theoretical material density. The liquid PS polymer LP-33 was purchased from Toray Fine Chemicals Company of Tokyo, Japan. LP-33 is a polymer of bis-(ethylene oxy) methane with mercaptan terminal end groups [27]. The PS formulations use an oxidative curing mechanism consisting of a combination of p-quinone dioxime and manganese dioxide with a total cure ratio of 10.4:1. Diphenyl guanidine is used as a cure catalyst in all five formulations. The elemental sulfur doping fraction ranges from 0.0 to 6.8% by mass. Also shown in the table are the peak mass loss temperatures of thermal decomposition as determined by TGA at a heating rate of 20 °C/min [3]. Of note in the table is that the measured Shore A hardness increases with sulfur content up to 1.8% but shows a decrease at 6.8%. As previously reported [3], the elemental sulfur acts to increase the cure ratio of the polymer as the mass fraction of sulfur increases tending towards higher Shore-A values. However, as the excess sulfur increases the number of high energy –S–S– bonds are replaced with lower energy –C–S_x–C– bonds tending to lower the Shore-A beyond a doping fraction of 1.8%. The net result is a peak in the Shore-A hardness at a sulfur content between 1.8 and 6.8%.

2.2. Pipe combustor configuration and procedure

The purpose of the pipe combustor test is to acquire ignition and mass burning rate data for fuel samples of controlled mass and surface area subject to an oxidizing flow parallel to the samples longitudinal face. A detailed view of the test setup is shown in Fig. 2. A Steinel HL-1910-E, 1500 W industrial heat gun with a

Table 1
LP-33 ramjet fuel formulations.

Ingredient	S0	Sp1	Sp5	S1	S4
Sulfur (% mass)	0.0	0.2	0.9	1.8	6.8
Sulfur to accelerant ratio	0.0	1.3	1.3	2.6	9.7
Cure ratio	10.4:1	10.4:1	10.4:1	10.4:1	10.4:1
Peak mass loss temperature (°C)	312.4	305.0	304.8	303.5	298.3
Shore A	15.0	38.0	43.0	44.7	38.3
Theoretical specific gravity	1.30	1.30	1.30	1.31	1.33

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