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Rheology of solid-like ethanol fuel for hybrid rockets: Effect of type and concentration of gellants

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ABSTRACT

This study reports first findings on the solidification of eco-friendly ethanol fuel by organic gellant, namely, Methylcellulose (MC) and Hydroxypropyl methylcellulose (HPMC) for use as a solid fuel for the hybrid propulsion system. Specifically, the rheological properties of solidified ethanol are determined using both shear flow tests and dynamic oscillation tests for the gellant concentration varying in the range of 5 wt% to 17 wt% and nanoparticle loading varying in the range of 2 wt% to 6 wt% for HPMC and 2 wt% to 4 wt% for MC samples respectively. It is observed that over the range of applied shear rate ($0.1–1000\ s^{-1}$) solidified ethanol fuels exhibit a strong shear thinning, high yield thixotropic behavior. The yield stress of the fuel sample ranges from 424.20–1252.40 Pa, and found to the direct function of type, concentration of gellant and nanoparticle loading. Below the yield stress, the solid samples exhibit an elastic dominant behavior ($G' > G''$) and found to be independent of applied stress in the linear viscoelastic region. In dynamic tests, the spectra of $G'(\omega)$ and $G''(\omega)$ indicates that solidified ethanol forms a covalently cross-linked network between ethanol-water blend and gellant material. A key finding of this study reveals that all ethanol fuel formulations display solid-like characteristics under test conditions as G' and G'' are nearly independent of the frequency and the magnitude of G' is 4.1–5.4 times higher than G''. Finally, the effect of gellant type on rheological behavior is studied where it is observed that the relative thixotropic area and creep strain of HPMC laden fuels is significantly higher compared to their MC counterparts which imparts them a viscous dominant character.

1. Introduction

The importance of rheological studies has grabbed recent attention in many fields ranging from food manufacturing, polymer science and pharmaceutical drug delivery to understanding the rheo-physical behavior of novel gellant based fuels for advanced propulsion systems [1–8]. Specifically, rheology has played a key role in understanding the mechanical behavior of complex functional fluids such as propellants, slurries and polymer solutions that display a wide spectrum of micro-structural arrangements. The rheological properties of the propellants should be studied in detail to understand their processability, storage life, flow characteristics during casting to obtain defect-free propellants. In practice, rocket propellants are primarily a blend of two or more components and their rheological characterization is important to understand the propellants response in real larger scale applications by correlating them with laboratory scale measurements [9]. Thus, from an application viewpoint, it is crucial to determine static rheological parameters such as apparent viscosity and yield stress (through simple shear flow) and time-dependent dynamic properties using oscillation tests. Similarly, hybrid rockets constitute chemical based propulsion with the fuel and the oxidizer in distinct phases that are physically separated. This usually consists of an inert solid fuel grain that is combusted by exposure to a high-pressure injection/feeding of a liquid or a gaseous oxidizer [10]. Hybrid rocket engines offer advantages of improved safety, minimal environmental impact and reliability which has made them a favorable choice for space exploration compared to traditional liquid or solid rockets. However, the available conventional fuels such as paraffin wax and Hydroxy-terminated Polybutadiene (HTPB) that are currently used as hybrid propellants have inherently low surface regression rates (r_b) specific impulse (I_{sp}) and low combustion efficiency (C^*_{eff}) [11,12]. The latter flaw was attributed by the incomplete mixing of oxidizer flow and fuel over the grain surface. Several methods such as multiport grain geometries, addition of metallic particles and even doping of small amounts of oxidizer in the inert fuel have been investigated by various

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researchers to improve combustion performance and accelerate fuel burn rates [13]. For instance, Nagata et al. [14] developed an axial flow end-burning hybrid rocket consisting of a series of stacked, cylindrical block of inert PMMA fuel grain separated by small space between the blocks. Their test results indicated that the fuel regressed was about twice as fast as the port and the combustion efficiency was 90%. However, a reduction in the overall volumetric efficiency of the fuel grain was reported for the configuration used in the study [14]. The effect of various metal powders on the r_b and C^*_{eff} of HTPB solid fuel was investigated in detail by Risha et al. [10]. They observed that a 62% increase in the mass burning rate at an estimated C^*_{eff} of 88–92% can be achieved with a fuel formulation having an active aluminum content of 84.8% compared to that of a neat fuel. However, a further increase in the aluminum content increased the mass burning rate but decreased the C^*_{eff}. In another study Strand et al. [15] tested and analyzed fuels consisting of 40% Al, 30% coal, and 30% HTPB to investigate the effect of metal particle combustion on the regression rate behavior. They found that metalized fuel regressed 17% faster than the pure HTPB due to the thermal radiation from metal particle combustion. However, high regression rates are not attractive if they are accompanied by low combustion efficiency. The limitations in the hybrid propellant can be overcome by thinking of an alternative fuel which is eco-friendly, cost effective and offers advantages of high energy density, high burn rates, and lower ignition delay. Ethanol is one such renewable biofuel that is environmental-friendly and has a long and illustrious record as an energy-efficient liquid rocket fuel: being the fuel for German V-2 and PGM-11 Redstone Rocket [16]. However, the direct utilization of ethanol in hybrid motors is constrained as it is in the liquid phase and hence it must be solidified using an appropriate thickener or a gelling agent. However, the C^*_{eff} is affected by the type of gelling agent used i.e. inert or energetic gellant. The use of energetic organic gelling agents such as cellulose derivatives [17,18], sorbitol or hydrogenated castor oil [19], improves the C^*_{eff} and heat of combustion (ΔH_c) since organic gelling agents are completely consumed (or burned) and contributes directly to combustion heat release process. As reported in Ref. [18], an increase in the gellant concentration (methylcellulose) by 7 wt% in solid ethanol increased ΔH_c by 3.25%. On the contrary, the use of inert gelling agents has an adverse effect on the C^*_{eff}. For instance, fumed silica, an inorganic inert gellant used for gelation of UDMH, JP-5 and Kerosene significantly affects the burn rate of the fuel since they remain unburnt [19]. Therefore, this study first focuses on selecting an appropriate organic gellant for ethanol and secondly, it illustrates how the rheophysical properties of the base fuel vary as a function of gellant type and concentration.

Solidification of fuels using gellant additives has been in practice, and a few studies have explained their effect for specific applications [20–23]. For instance, Geller discovered that solid alcohol made from sodium salts of aromatic acids could be used for manufacturing solid spirit. He also observed that the addition of cellulose based derivatives could improve the chemical stability of alcohols [20]. Monick [21] formulated solid-alcohols for combustion based applications by adding water along with cellulose derivate to smaller chain alcohols. Their application was however restricted to domestic fires where the rheological properties or thermodynamic conditions had little role to play [23]. Larson et al. reported solidification through cryogenic freezing of organic liquids and observed a 3–4 times increase in the regression rate compared to a solid HTPB grain under the same oxidizer mass flux condition [24,25]. In a similar study, Gramer et al. conducted tests using solidified kerosene and methane combusted with gaseous oxygen. They observed 20–40 times higher regression rate relative to the HTPB-based fuels [26]. Karabeyoglu et al. also observed a higher regression rate for solid cryogenic fuels made from pentane, methane, oxygen and non-cryogenic wax compared to the conventional hybrid fuel. However, the stability of the liquid layer formed over the melt region (on the surface of solid charge under actual pressure condition) is a concern and the complex methodology involved in making solid cryogenic fuels is both uneconomical and possess practical difficulties [27,28]. Consequently, Brandenburg employed a mixture of Plexiglass, gelled ethanol made from methylcellulose in conjunction with calcium acetate, as a solid fuel, and nitrous oxide as the oxidizer. For this tri-component fuel, the I_{sp} improved by $\sim 6\%$ (on an average) at 1100 psi from the static motor firing [16]. Although these studies dealt with performance-based tests, they lacked details on the stability and mechanical properties of test fuels.

In this paper, efforts are put forward to solidify ethanol using an organic gellant and to characterize the solid-like ethanol fuel using rheology. The linkage between the rheological properties and combustion performance has been reported by Galfetti et al. [29] in a paraffin melt layer. They observed a strong correlation between the measured viscosity of the melted layer and the surface regression rate which can be explained as follows: When subjected to shear, a hydrodynamically unstable thin liquid layer is formed over the surface of the melt (due to shear thinning property) which tends to break up the melt layer into ligaments and further into finer droplets. As the oxidizer gas stream is then injected at high pressure, these droplets are entrained which speeds up the surface regression. Since the ligament formation and break-up process is accelerated with a reduction in viscosity, the shear thinning behavior indeed facilitates an enhanced combustion performance (by decreasing melt layers viscosity by several orders of magnitude). Thus, a decrease in viscosity of the solid propellant with applied shear translates directly to a higher regression rate. This forms one of the key ideas of the present study i.e. to formulate a hybrid propellant that exhibits shear-thinning characteristics.

Solidification of ethanol is achieved by means of gelation technique i.e. a physical process which involves the formation of a three-dimensional network within the liquid fuel. Though rheology is widely used to characterize gel fuels, literature search reveals that there is a dearth of information on the experimental analysis involving rheological characterization of solid-like materials. The process of gel fuel formulation is similar to that of solid fuel but differs only in terms of the amount of gelling agent being added. As such, the gellant concentration largely ascertains the phase of the fuel and with increasing concentration the phase transitions from gel to semi-solid to solid-like to finally a perfect solid. It is important to note that the rheological properties are intrinsically dependent on the three-dimensional network of the fuel which in turn is affected by the gellant concentration. Gelled fuels can be classified based on several parameters such as flow index (shear-thinning), yield stress (strong or weak) and viscoelastic properties [30–34]. Since an understanding of flow behavior of fuels is of primary concern in propulsion applications, the shear thinning thixotropic behavior has been studied extensively for gel fuels. Thixotropy is a time-dependent rheological property that plays a crucial role during feeding and atomization for gel fuels [33–36]. Moreover, for hybrid rockets, thixotropy provides insights into the structure recovery (to a stable solid phase) once the shear applied by the oxidizer is removed during the rocket on-off stage operations. A qualitative evaluation by Rahimi and Natan [32] showed that the thixotropic effect in propellants depends primarily on the type of gellant i.e. inorganic or organic. For instance, if the gellant carries hydrophobic units, it aids in the network formation at the molecular level, and the thixotropic effect is prominent. For example, a significant thixotropic behavior was observed by Maestro et al. in hydrophobically modified hydroxyethyl cellulose