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Ignition Characteristics of a New High-Energy Density Fuel in High-Speed Flows

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Polycyclic undane alkene dimers, $C_{22}H_{24}$ are members of a new class of high-energy-density hydrocarbon fuels. Their ignition characteristics have been evaluated as solid fuels under conditions of high shear flow. Samples of the dimer were cured with a styrene-polybutadiene copolymer (10% w/w) binder on the test chamber wall and convectively ignited by a gaseous flame in air at Mach 0.12–0.25, stagnation temperature and pressure of 300 K and 150–250 kPa, respectively. Ignition times and rates of heat release were measured. The results indicate that compared with hydroxy-terminated-polybutadiene fuel at the same thermodynamic conditions and geometrical configuration the dimer ignition times are one order of magnitude faster. The heat released by combustion by the dimers is more than twice as large. Phase change, ignition, and combustion processes of these fuels are investigated with the aid of scanning electron microscope, high-speed photography, and pressure and temperature measurements.

Introduction

POLYCYCLIC undane (PCU) alkene dimers, $C_{22}H_{24}$, are highly dense fuels ($\rho = 1.2$–1.3 g/cm^3) and exhibit very large heat of formation (+231.5 kJ/mol).[1–3] These compounds are of interest as high-energy fuels or fuel additives, with the expectation that their inclusion in the fuel mixture will result in a net increase in volumetric efficiency of the current generation of powerplants. The synthesis of these hydrocarbons is very recent and a complete set of property data, including the amount of strain in the bonds, is not available at present. These high-energy-density materials are stable under ambient conditions, a fact that renders them suitable for long-term storage at room temperature and further ensures simple operational logistics for a broad range of applications. A configuration of particular interest is that of a solid-fueled ramjet (SFRJ). A problem related to the operation of these devices is ignition and stability of the flame at low pressures and high crossflow velocities. In a typical SFRJ flowfield the balance between the competing mechanisms of heat transfer to the fuel (by convection and, unlike in rocket motors,[4] in a lower proportion by radiation[5]) and convective transport from the surface is strongly influenced by the local thermodynamic conditions, the thermodynamic and transport properties of the fuel, and the binder[6] and the boundary conditions, the presence and the size of recirculations regions, incoming freestream gas temperature, and the chemical composition of the pool of free radicals in the reaction region. Ramjets, unlike rocket motors, operate at low internal pressures (several atmospheres) and relatively large crossflow airspeed. Under these conditions conventional hydrocarbon fuels are difficult to ignite.[7] The ignition delay time τ_{ig} as well as the chemical reaction rates for hydrocarbons are both adversely affected by the low pressure in the combustion region[5]: the ignition delay time is inversely proportional to pressure, whereas the pyrolysis rate of the solid fuel and the exothermic reaction rate (assuming a global, homogeneous reaction) grow according to a power law dependency on the local pressure, via the mechanisms described for erosive burning. High-energy-density fuels have the potential to offer substantial rates of heat release in the combustion region that balances in part the lengthening of the reaction rates as a result of the low pressure and convection of reacting species from the region. Reference 7 indicates that combustion of solid high-energy-density fuels can be sustained even under supersonic crossflow conditions. Nevertheless, ignition and stable combustion are difficult to achieve in high-speed flows. Piloted ignition generated by a gaseous flame can provide the system with the energy required to ignite and sustain steady combustion of the solid grain. An accurate evaluation of the effect of the heat flux from the ignition source to the fuel is complicated by the presence of chemical sources (mostly from free radicals, H, O, OH, etc.) in the igniting flux in comparison with ignition via a radiant heat flux. This method, however, is representative of SFRJ operation and was, thus, employed in this study. To minimize the complexity of such a system the ignition source was provided by a hydrogen pilot flame.

The interactions between fluid dynamics and chemical kinetics have a significant effect on the global flow parameters and the burning rates. These mechanisms cannot be addressed in an uncoupled manner in this application since the chemical reaction rates and the fluid residence time are comparable. Gasification and subsequent mixing determine the rates of heat release, which, in turn, affect the phase change at the solid-gas interface and the reaction rates. Comparisons with combustion of hydroxy-terminated-polybutadiene (HTPB) at the same conditions and geometry and with other published data of other propellants clearly indicate this interdependence and the need to evaluate combustion and fluid mechanics as a unified system.

Description of the Fuel

The high-energy-density fuel employed in the present study is a mixture of the four isomeric PCU alkene dimers (Figs.

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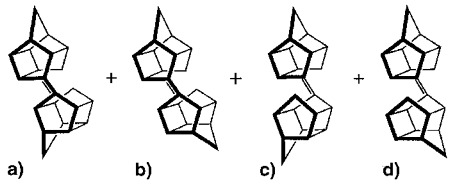

Fig. 1 PCU alkene dimers structure.

1a–1d) whose structures are shown in Fig. 1. These hydrocarbons have been synthesized via titanium-promoted reductive dimerization of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one.[1,2] The calculated heat of formation ΔH_f is +231.5 kJ/mol and the corresponding calculated heat of combustion is 41 kJ/mol. A certain degree of strain is present, but this strain energy has only a minor contribution to the energy output during combustion. Their heat of formation is remarkable when compared with other high-energy hydrocarbons, e.g., benzevalene (C_6H_6, ΔH_f = +377 kJ/mol) and dihydrobenzevalene (C_6H_8, ΔH_f = +240 kJ/mol), which have a considerable strained configuration. The density of each isomer falls within the range 1.2–1.3 g/cm^3, thereby rendering Figs. 1a–1d of particular interest as high-energy-density fuels for volume-limited applications. The synthesis of these novel compounds has been described elsewhere.[1,8]

Experimental Apparatus and Test Conditions

A schematic of the facility is shown in Fig. 2. The test section has a constant cross section of 3.8 × 2 cm and is 17 cm long. Quartz windows installed on the walls of the test section provide optical access to the flowfield. A choked orifice is placed at the exit to control the test section entrance velocity. The wall including the fuel sample and the wall opposing it are instrumented with pressure taps and K-type thermocouples imbedded at 0.1 mm below the surface. These thermocouples measure local flow temperatures and provide an indication of the heat released during combustion. At the test section entrance, gaseous hydrogen is injected via five transverse orifices with a total cross section area of 1.8 mm^2 and ignited with an electric discharge. Hydrogen mass flows are then correlated with the airflow experimental conditions to determine the heat flux to the solid fuel surface, as described in a following section. In the following, the values of the heat fluxes are used, rather than the hydrogen mass flows, since heat fluxes are more relevant for the solid fuel ignition process.

The fuel was placed on the test section wall using a styrene–butadiene copolymer dissolved in toluene as a binder. The solid fuel was ground to a fine powder, mixed with the binder and cured at room temperature for 24 h. As tested, the sample contained 10% binder weight/weight. The sample was shaped as a circular arc with a thickness of 5 mm at the center, a total length of 7.5 cm, and a constant cross section in the transverse direction. HTPB samples of the same shape were prepared following the procedure described in Ref. 9.

Wall pressures were measured with an electronic pressure scanner PSI® 9020 and referenced to a high-accuracy pressure transducer MENSOR® DPGII with an overall accuracy of 0.08%FS. A charge-coupled device DALSA® camera was used to measure the ignition time. The camera is equipped with a 128 × 128 pixel sensor and operated at a frequency of 125 frames/s. During the experiment the camera was triggered by the ignition of the gaseous pilot-flame, which has a negligibly small initiation time in comparison with that of the solid fuel. The ignition time of the solid fuel was measured from initiation to the first frame that indicates luminous ignition of the dimer. There was a bright emission from the solid fuel combustion, as expected for a fuel with a low hydrogen to carbon ratio as the PCU alkene dimers that clearly separated the combustion of the fuel from the hydrogen flame. The experiments took place at test section entrance stagnation pressure P_0 = 150–250 kPa, stagnation temperature T_0 = 298 K, and Mach number at the fuel location of 0.12 and 0.25, which are representative conditions for ramjet operation at low altitude and high, subsonic speed.

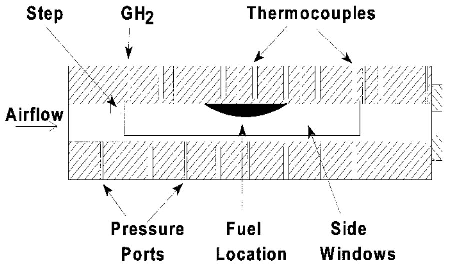

Fig. 2 Test section schematic, side view.

Heat fluxes were calculated with a simplified model where complete combustion of the hydrogen–air mixture took place and the sample surface temperature remained constant. With this assumption, the estimated fluid temperature at the solid fuel surface ranged between 600–1200 K, depending on the selected equivalence ratio. For comparison, a two-dimensional equilibrium calculation was performed to determine the temperature distribution in a plane perpendicular to the sample, in the flow direction. The equilibrium assumption for the hydrogen–air combustion was justifiable in this case, since the hydrogen ignition delay times were estimated to be approximately 0.1 ms (Ref. 10), whereas the residence times were 0.6 ms. This calculation indicated a typical isotherm at the solid fuel surface of 750 K, in general agreement with experimental observations. For these experiments, the temperature of the solid fuel was assumed constant at 298 K. In previous studies[11] it was assumed that the surface of the solid fuel melts and maintains a constant solid fuel surface temperature during combustion. In reality, the temperature of the solid phase surface changes in time from the initial value (298 K in this case) to the melting point (450 K for the PCU alkene dimer). Chemical transformations at the interface layer can be present, contributing to the phase change and affecting the temperature.

Results and Discussion

Ignition Times

Figure 3 shows the measured ignition times as a function of the convective heat flux $\bar{h}_f$ calculated from uniform mixing and complete combustion of the gaseous flame by estimating the average Nusselt number for turbulent flow over a flat plate[12]:

$$N\bar{u}_x = 0.037(Re_x)^{0.8}(Pr)^{0.33}$$

The ignition time was measured from the time of the initiation of the gaseous flame (negligibly small in comparison with the dimer) and the first indication of light emission from the solid fuel. Shown in the figure are the ignition times compared with previously reported data for solid fuels based on ammonium perchlorate (AP)[13] and cyclotrimethylenetrinitramine (RDX).[11] There are substantial differences between the different sets of data for the same externally applied heat fluxes and similar incoming gas velocities. These differences cannot be accounted for only by the different fuel composition or by the differences in the convective gas composition. Differences in the fluid velocity across the solid sample cannot explain the large differences in the ignition times either, since, as shown in Ref. 13, changes in velocity from Mach 0.2 to 1.0 for the same applied heat flux result in only 30–40% increase in the ignition time. It appears that a major role is played by the selected geometry of the solid fuel sample and the presence of recirculation regions, where the fluid residence time is long

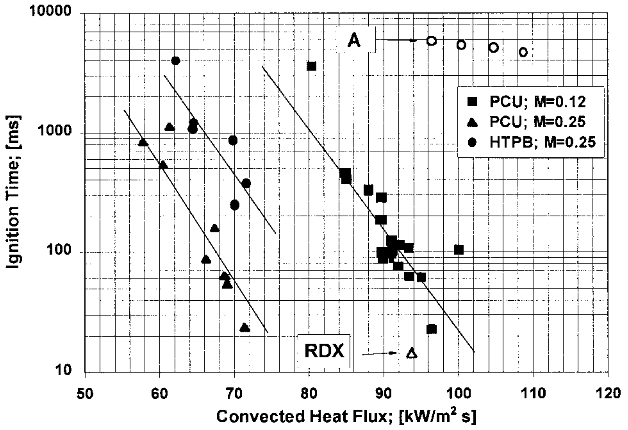

Fig. 3 Ignition times vs heat flux.

and the heat transferred to the solid fuel is substantial. Although the experiments in Ref. 13 took place at essentially the same crossflow velocity as in the present work the fuel sample was flush with the test section wall therefore no recirculation regions were present. Alternatively, the experiments in Ref. 11, although conducted at similar heat fluxes and inlet velocities, exhibited large recirculation regions downstream of the cylindrical fuel sample where, locally, the velocity was substantially lower than the freestream, the heat transfer was accelerated, and the residence time increased. To obtain a more meaningful measurement, samples of HTPB were cured at the same geometrical configuration as the PCU alkene dimer and ignited at same airflow thermodynamic conditions. The results are shown in Fig. 3 and indicate that the PCU alkene dimer has one order of magnitude faster ignition than HTPB.

Once ignited, the flame developed rapidly, extending upstream along the fuel sample. Note that in all cases the PCU did not self-sustain once the pilot flame was removed. The issue of flame self-sustaining and the amount of piloted-energy required for ignition and subsequent flame stabilization is subject to configuration optimization and is not addressed by the present study.

Heat Release

Figure 4 compares the heat released by the combustion of the dimer with the heat produced during combustion of hydrogen only and the combustion of HTPB. Indicated in the figure are the location and the geometry of the solid fuel. The curves were selected at $t = 1.5$ s after the initiation of the pilot flame. The combustion of the HTPB sample, including the contribution of both the hydrogen pilot and HTPB, produced only a small increase in temperature relative to the pilot flame alone case. The curve corresponding to the dimer combustion experiment, however, shows a substantially stronger heat release. This plot reflects the heat transferred to the experimental apparatus walls and indicates in a qualitative manner the significantly larger amount of heat contributed to the airflow by the PCU alkene dimer.

The samples mass losses were not measured after the experiment and, in fact, there is no guarantee that even if the fuel vaporizes, complete combustion will take place within the apparatus, thus, a quantitative measurement of heat deposition cannot be, in general, provided by this type of experiment. However, the mass loss of the partially burned samples of PCU and HTPB were comparable. This study was concerned with the ignition times of the PCU and it indicated that they are substantially larger than HTPB, which was selected for comparison. This conclusion is significant, because high-energy materials are often characterized by a low reactivity. The ignition time is, clearly, influenced by the increased energy released in the flow by increasing the flux of heat that is transferred back to the fuel. The regression rate would be influenced by these factors as well. The heat provided by the hydrogen flame was controlled and kept constant between the experiments with PCU and HTPB shown in Fig. 4, thus the hydrogen contribution was the same in both cases.

Photographs of the sample before and after combustion are shown in Figs. 5a–5c, taken with the scanning electron microscope at magnifications of ×2000. The surface of unburned fuel in Fig. 5a shows a very convoluted region. There was no attempt during these tests to polish the fuel surface, and the surface roughness can contribute substantially to accelerate the melting and subsequent gasification of the irregularities at the sample surface, hence accelerating the global reactions. However, these irregularities do not contribute sensibly to the heat

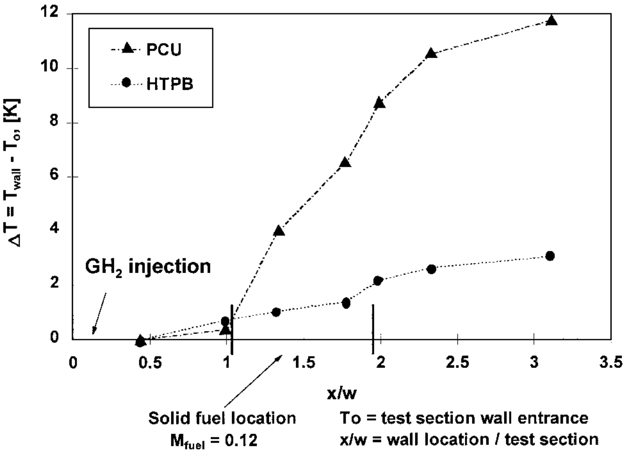

Fig. 4 Wall temperature distribution.

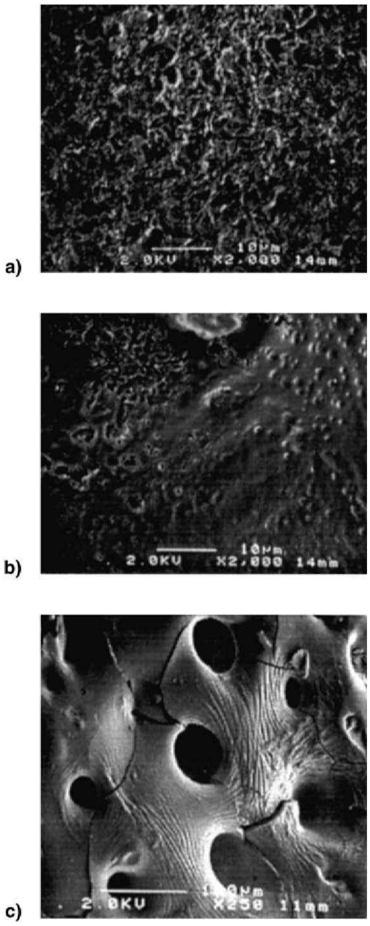

Fig. 5 Surface quality pre- and postcombustion analysis: a), b) fuel, and c) binder.

deposition as they disappear within the initial stage of melting and pyrolysis. This surface structure is in strong contrast to the image in Fig. 5b, which is a photograph of a burned fuel surface, that is clearly smoother because of melting. Figure 5b shows the formation of small craters with a diameter of about 1 μm, an indication of surface boiling. These surface modifications cannot be attributed to the binder since the copolymer exhibits quite different surface characteristics, as shown in Fig. 5. Large craters were formed by the boiling of the polymer; cracks and wrinkles in the surface resulting from melting and resolidification are noticeable, however, the smooth nature of the surface is, in general, preserved.

Summary and Conclusions

The results of the ignition experiments at high convective rates of the PCU alkene dimers indicated the following:

1) Measured ignition times are one order of magnitude faster than for HTPB at the same geometrical and thermodynamic conditions. Fuel surface roughness did not play a significant role in the determination of the ignition times.

2) The heat released during combustion was more than twice as large for the PCU alkene dimers than for HTPB. Post-test analysis of the PCU alkene dimer and HTPB samples indicated similar mass loss. This is not, however, a direct indication of the heat deposition in the airflow since completeness of chemical reactions within the test apparatus cannot be guaranteed. The heat transferred to the walls is a better indication of the differences in the energetic capabilities of the two materials.

3) There is evidence that ignition and subsequent combustion develops and continues in a gaseous phase in regions of long fluid residence (separation regions).

4) The flame did not self-sustain following ignition: removal of the high-temperature incoming gas resulted in all cases in flameout. The issue of flame sustainability is the subject of configuration optimization.

5) Microscopic inspection indicates clearly that melting of the surface layer is present. The effect is mostly caused by physical transformation, however, chemical reactions can contribute to the phase change.

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