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Droplet Combustion, Microexplosion, and Sooting Characteristics of Several Energetic Liquid Propellants

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The combustion characteristics of droplets of four newly synthesized energetic fuels, namely, 1) 1,4-dimethyl ester cubane (which is a solid slightly soluble in conventional liquid fuels), 2) dihydrobenzvalene, 3) phenyl azide, and 4) carborane (which are all liquids), were experimentally identified and quantified. Results show that the gradual concentration and eventual condensation of dimethyl ester cubane dissolved in benzene can lead to strong droplet microexplosion; that the three liquid fuels all soot profusely, with the sooting propensity, when compared with other fuels, being in the following order: JP-10 < benzene ≈ dihydrobenzvalene < phenyl azide < carborane; and that phenyl azide additionally exhibits fast gasification rates, advanced microexplosion events, and sensitivity to halide addition. It is emphasized that a high-energy-density fuel does not automatically imply that it is fast burning, and that it must also possess desirable combustion characteristics, especially minimal sooting formation, before it can be considered for use as a jet fuel or jet fuel additive.

Introduction

THE interest in the development of compact, high-specific-impulse, liquid-fueled propulsion devices for combat applications has stimulated synthesis of high-energy-density liquid propellants and corresponding studies of their combustion characteristics. The desirable characteristics of such propellants are 1) high energy density on both mass and volume bases, 2) fast burning rate in terms of the global heat release rate by considering both the heterogeneous and homogeneous processes, and 3) other auxiliary favorable burning characteristics, such as minimal soot formation for reduced thermal loading on the combustor liner and for enhanced burnout of the fuel. It is of particular significance that a fuel possessing a high-energy density does not automatically imply that it has a fast burning rate. Indeed, because it is well recognized that the dominant burning mode within such liquid-fueled combustors is spray combustion, which is intimately affected by the physical processes of droplet gasification and fuel–air mixing, a faster gas-phase reaction rate resulting from the higher energy content of the fuel may not lead to a correspondingly higher global heat release rate.

Recently, a class of energetic liquid materials, consisting of diazidoalkanes and diazidoalkanols, have been synthesized[1] and demonstrated to exhibit exceptionally high droplet gasification rates that can exceed those of regular hydrocarbons by an order of magnitude. This greatly enhanced gasification rate is a result of the presence of liquid-phase reactions, whose heat release not only reduces the diffusive heat transport from the gas phase to effect a phase change at the droplet surface, but can also induce droplet microexplosion caused by internal gas release through either chemical reaction or superheating. The gasification rate can be further increased through either pressure elevation or the addition of small quantities of organic dihalides.[2]

The high-energy content of the azides is derived from the breaking of the $N-N_2$ bond, releasing about 50 kcal/mole of heat. There are, however, alternate means of increasing the energy content of the fuel. One approach is to increase the strain energy of the bonds between the carbon atoms, which frequently results in a tight molecular structure with a high carbon-to-hydrogen ratio. Examples are benzvalene (C_6H_6) and cubane (C_8H_8), whose molecular structures are shown in Fig. 1, as well as their derivatives. Note that the carbon-to-hydrogen ratios of benzvalene and cubane are 1, as compared to values close to 0.5 for many conventional hydrocarbon fuels. The second approach is to add elements with high heats of combustion into the molecular structure of the hydrocarbon fuel. An example is the carborane family of compounds, in which boron atoms are present in the fuel molecule. The oxidation of boron gives the higher heat content of these fuels.

In this paper, we report the droplet combustion characteristics of four energetic materials synthesized and made available to us, namely, 1) 1,4-dimethyl ester cubane, 2) dihydrobenzvalene, 3) phenyl azide, and 4) a carborane compound, with phenyl azide exhibiting enhanced gasification rates and advanced microexplosion states. Perhaps the most significant result from the present study is the identification and thus recognition that many of the synthesized and proposed energetic liquid materials have high propensity for soot formation. This deleterious effect must be properly taken into consideration when synthesizing and deploying new energetic materials.

We will first briefly discuss the experimental setup used in the investigation of droplet combustion of these materials. We will then sequentially present results of these four compounds, demonstrating the unique combustion characteristics of each.

Experimental Methodology

Details of the experimental apparatus and procedure are given in Refs. 1 and 3. Figure 2 shows a schematic of the apparatus. In the experimentation, a single monodisperse stream of droplets, generated by a piezoceramic crystal using the ink-jet printing technique, was axially injected downward into the postcombustion region of a premixed, flat-flame burner. The droplet size for the experiments was about 290 μm. The droplet spacing was about 100 droplet diameters, so that droplet interaction was negligible. The droplet Reynolds number was estimated to be around 1. The composition of the gaseous mixture fed to the burner was controlled to yield a

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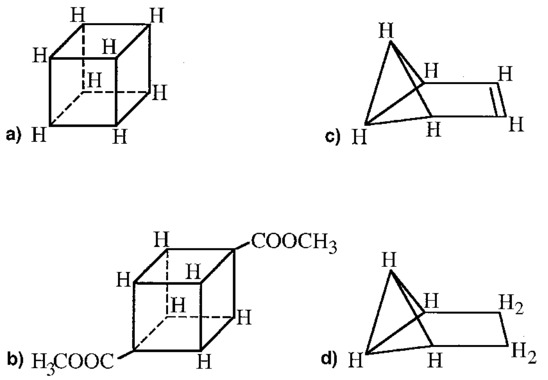

Fig. 1 Molecular structures of a) cubane, b) 1,4-dimethyl ester cubane, c) benzvalene, and d) dihydrobenzvalene.

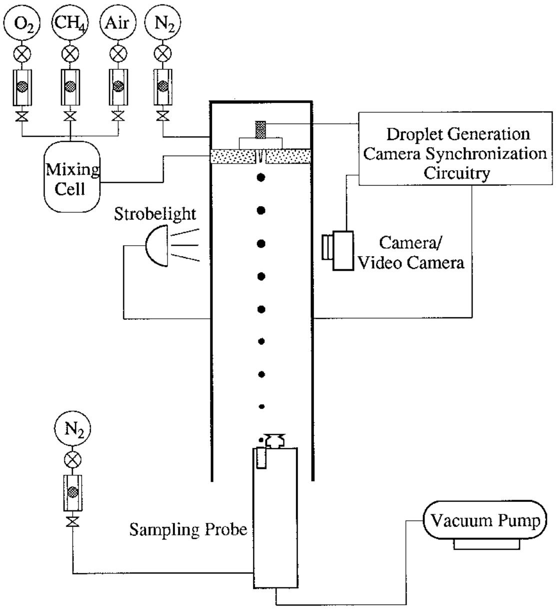

Fig. 2 Schematic of the experimental apparatus.

combustion environment of specified temperature, which typically varied between 980 and 1040 K along the distance over which the droplet gasification took place. The environment oxygen concentration was 21 mole% for combustion studies and was 0 for pure vaporization studies. The chamber pressure could also be varied up to about 5 atm.

Droplet and flame size histories were determined with a stereomicroscope and a variable time-delay strobe flash synchronized with the droplet generation circuitry. The instantaneous soot samples were obtained by laterally sucking away the gas-phase components surrounding the droplet, quenching and cooling it immediately by nitrogen flow. These gas-phase compounds were further passed through a filter that was subsequently dried and weighed for the soot mass collected.

Results and Discussions

Combustion of 1,4-Dimethyl Ester Cubane

1,4-dimethyl ester cubane (Fig. 1) is a solid component at room temperature. It can dissolve in benzene and toluene up to 4.5 mass% and is sparingly soluble in JP-10, alkanes, and alcohols. The experiment was run with its saturated solution in benzene, consisting of 4.5% of cubane.

Figure 3 shows a typical d^2-law plot of the droplet burning history, which is terminated by the onset of microexplosion. The results show that, after the initial period of droplet heating, d^2-law is followed quite well. The burning rate constant, $K = -\mathrm{d}(d_s^2)/\mathrm{d}t$, is 0.88 mm^2/s and is close to the value of benzene at the same experimental conditions. This indicates that during the period of droplet burning, only the volatile component, benzene, is gasified, leaving the less volatile component, cubane, in the droplet. Consequently, the concentration of cubane in the droplet should increase as burning progresses. To substantiate this possibility, droplets were sampled. Figure 4 shows that the cubane concentration in the droplet continuously increases with time. Before the state of microexplosion, the cubane concentration reaches 14%. To identify the significance of this value, Fig. 5 plots the solubility of cubane in benzene as a function of the solution temperature, recognizing that the droplet temperature will also continuously increase as

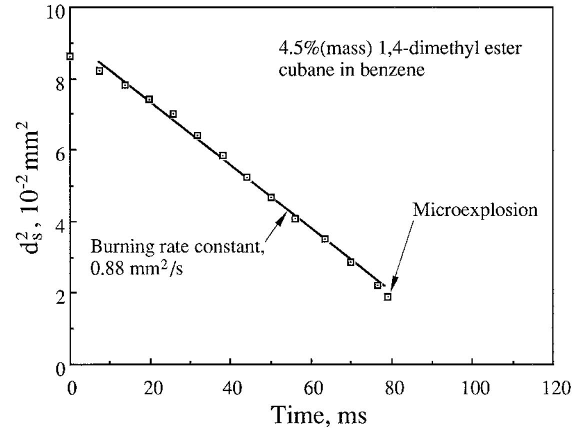

Fig. 3 d^2-law plot for the droplet burning of 1,4-dimethyl ester cubane in benzene.

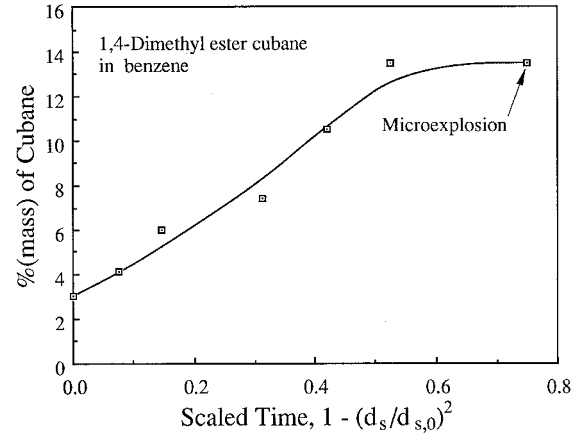

Fig. 4 Temporal concentration variation of 1,4-dimethyl ester cubane in benzene during droplet burning.

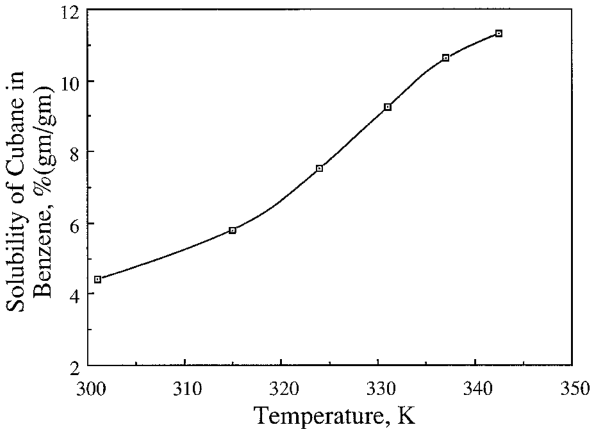

Fig. 5 Solubility of 1,4-dimethyl ester cubane in benzene.

burning is initiated until the equilibrium vaporization temperature, which is slightly below the boiling point of the liquid, is reached. This implies that the droplet can dissolve more cubane from its initial saturated value as it is heated. Figure 5 shows the continuous increasing trend of the solubility of cubane in benzene with increasing temperature, reaching a solubility of 11.5% at the boiling point of benzene. Recognizing that this value is just slightly below the sampled droplet composition of 14% at microexplosion, and that some degree of supersaturation must exist before nucleation of the solid cubane takes place, the following combustion mechanism of the cubane/benzene solution is suggested. During the period of droplet lifetime, the bulk gasification basically involves that of the more volatile component, benzene, causing the concentration of the nonvolatile component, cubane, to increase. Because the droplet temperature continuously increases, the cubane can remain in the droplet until the droplet temperature reaches the boiling point of benzene. Continuous gasification causes the cubane concentration to exceed its maximum solubility at the boiling point of benzene. The supersaturated cubane eventually condenses out of the solution and initiates the droplet microexplosion.

Based on the preceding results, it seems that this cubane is suitable for use as a jet fuel additive, not only for its higher energy content, but also because it facilitates droplet microexplosion.

Soot Formation in Dihydrobenzvalene

Benzvalene has been proposed to be a strong candidate as an energetic liquid material. However, as suggested earlier, it is also expected to be a heavy soot-producing fuel because of its high carbon-to-hydrogen ratio.

Experimentation with benzvalene was not possible because of its unavailability. Instead, we were supplied with a mixture of benzene and a derivative of benzvalene, namely dihydrobenzvalene, whose molecular structure is shown in Fig. 1. Dihydrobenzvalene is easier to synthesize and is expected to simulate well the sooting tendency of benzvalene. The burning and sooting characteristics of a mixture of 20% benzene and 80% dihydrobenzvalene were thus determined and compared with those of JP-10, benzene, and phenyl azide. Figure 6 shows the droplet size histories plotted in the d^2-law format. It is seen that the burning rates of JP-10, benzene, and 80% dihydrobenzvalene are fairly close to each other as well as the well-established values for the alkanes. Dihydrobenzvalene does exhibit microexplosion, though fairly late in the droplet lifetime.

Figure 7 shows the instantaneous amount of soot that is present around a droplet, termed the soot index, as a function of the time normalized by the droplet lifetime assuming a d^2-law burning rate, where $d_{s,o}$ is the initial droplet diameter. It is seen that as the droplet burns, the amount of soot surrounding the droplet first increases and then decreases. This follows the same trend as that for the droplet flame size, indicating the reasonable relation between the amount of soot formed and the volume of the flame, and is in agreement with previous studies on soot formation in droplet burning.[3] Perhaps the most significant result here is that the sooting propensity of the dihydrobenzvalene mixture is about the same as that of benzene, and is higher than that of JP-10 by a factor of 5. We have therefore demonstrated conclusively that soot production is a serious problem with the use of the benzvalene-class of energetic fuels.

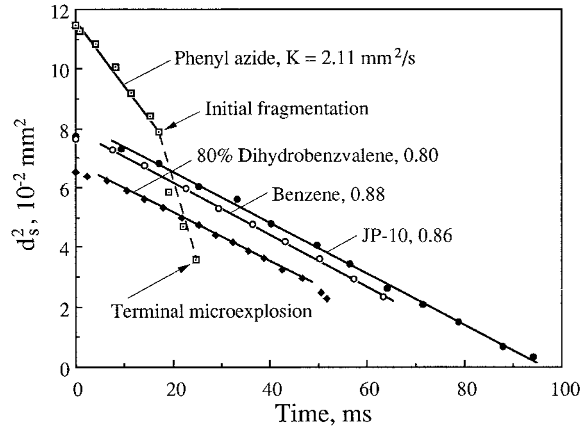

Fig. 6 d^2-law plots for the droplet burning of phenyl azide, JP-10, benzene, and dihydrobenzvalene.

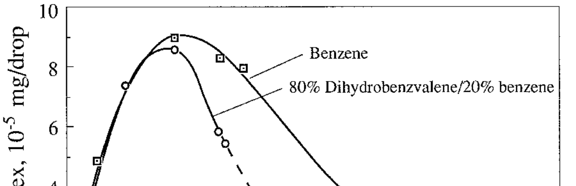

Fig. 7 Variation of the soot index as a function of scaled time for benzene, dihydrobenzvalene, and JP-10.

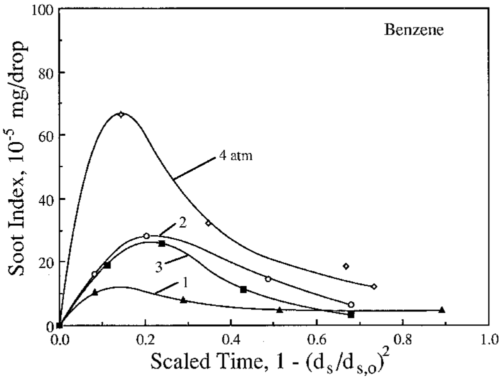

Fig. 8 Variation of the soot index as a function of scaled time for benzene at various pressures.

Because it is also generally recognized that the extent of soot formation increases sensitively with increasing pressure, and because the pressure within tactical aeroengines can range from high subatmospheric to superatmospheric, it is of practical importance to assess such a dependence. Figure 8 shows the soot index for pressures ranging from 1 to 4 atm. The same initial droplet size was approximately maintained for different experiments, so that the flame size variation was also about the same for different pressures. This minimized the effect of flame volume on soot formation and the results obtained would mainly reflect the chemical effect. The results demonstrate that increasing pressure significantly increases the amount of soot formed. Visually, in all experiments, soot breakthrough in the form of long strings[3] was observed.

Combustion and Microexplosion of Phenyl Azide

Recognizing the strong sooting propensity of benzvalene fuels, approaches toward minimizing soot production must be implemented before such fuels can be considered for use in tactical combustors. Because it is well established that soot formation is greatly reduced via premixed rather than diffusional burning, it appears that a viable approach is to enhance the rate of droplet gasification and consequently the rate of fuel/air mixing. From the results of azidoalkanes,[1,2] it is then reasonable to suggest that the droplet gasification rate could be greatly facilitated by attaching azido groups into the molecular structure of the benzvalene fuels. Again using benzene as a surrogate for benzvalene, a sample of phenyl azide (or azidobenzene) has been synthesized and tested, yielding the following combustion and microexplosion characteristics.

Figure 9a shows a representative flame streak of a burning droplet stream of phenyl azide. The upper, smooth, straight streak represents the ignition and steady burning period, while the lower portion, characterized by multiple streaks, represents the microexplosion and eventual burnout events. The length of the straight streak yields the steady-state burning rate, with the flame color being yellowish, indicating the strong intensity of soot formation of the test fuel. For comparison, the flame streak of benzene is shown in Fig. 9b. Compared with phenyl azide, the flame streak of benzene is long and narrows smoothly and slowly until burnout. For phenyl azide, the length of the entire burning and microexplosion event is considerably shorter, indicating increased overall burning rate and thereby reduced burning time. Compared to the previous microexplosion results on diazidoalkanes,[1] the difference is the characteristic of microexplosion. For the diazidoalkanes, particularly the heavy ones, the distorted droplet gradually becomes blob-like and continually loses small fragments of mass for a period of time. The droplet finally expands rapidly and strong microexplosion breaks it into tiny pieces. For phenyl azide, the droplet suddenly explodes following distortion, breaking into several droplets of moderately large sizes. It can be seen from Fig. 9a that these fragments continually burn for a while, followed by further microexplosion. The flame streak of phenyl azide appears yellow-orange and many black spots can be observed from the microscope. A long, extinguished tail is observed visually after the droplet microexplodes and black soot particles are found, again indicating the strong tendency of soot formation when the fuel burns in the diffusion flame mode.

Figure 6 shows that the steady burning rate of phenyl azide is substantially higher than that of JP-10, benzene, and the 80% dihydrobenzvalene/20% benzene mixture. Indeed, the burning rate constant, 2.11 mm^2/s, is similar to that of diazidononane.[1] It also shows that the phenyl azide droplet experiences fragmentation more than once, as just described.

Figure 10 plots the vaporization rate constant K as a function of pressure for phenyl azide, and shows that K increases fairly sensitively with increasing pressure. In accordance with our understanding of the combustion of diazidoalkanes,[1] this sensitive increase could imply the presence of liquid-phase reactions that are facilitated with increasing system pressure because of the corresponding increase in the liquid boiling point and, hence, in the attainable droplet temperature.

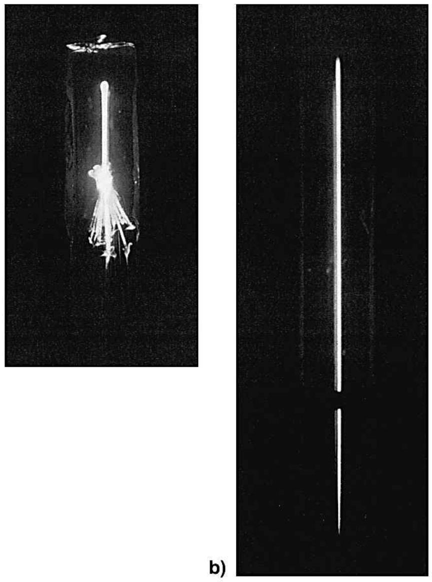

Fig. 9 Time-exposed photographic image of the flame streaks of burning droplets of a) phenyl azide and b) benzene. The break in the flame streak for benzene is caused by a physical viewing obstruction of the chamber.

To identify the benefit of microexplosion on the enhancement of the gasification rate, Fig. 10 plots the normalized droplet explosion size $d_{s,\mathrm{ex}}/d_{s,o}$, and the overall gasification rate

$$K' = K/[1 - (d_{s,\mathrm{ex}}/d_{s,o})^2]$$

vs the system pressure. It is seen that microexplosion occurs earlier with increasing pressure. Consequently, the K' at 4 atm exceeds that at 1 atm by a factor of 3. This facilitation of microexplosion is again an indication of the occurrence of liquid-phase reaction.

Experiments were also conducted for mixtures of phenyl azide with alkanes and halides to identify any possible catalytic effect as observed previously for mixtures of diazido- and dihalidoalkanes.[2] Because microexplosion of multicomponent droplets is strongly influenced by the volatility differential between the constituents,[4] additives with similar volatilities as that of phenyl azide were chosen to isolate the influence caused by liquid-phase reaction. They are n-decane, 1-bromoheptane, and 1,5-dichloropentane. For studies of volatility effects, n-hexadecane was chosen, whose volatility is substantially different from that of phenyl azide. Figure 11 shows that for binary mixtures of 25 mass% phenyl azide with 75% decane and hexadecane, respectively, burning rates for both mixtures

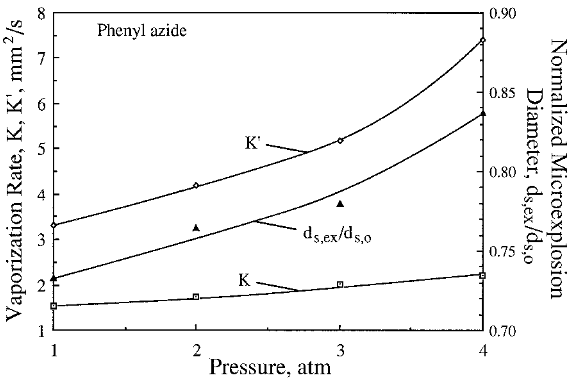

Fig. 10 Variations of the vaporization rate constant K, normalized droplet microexplosion diameter $d_{s,\mathrm{ex}}/d_{s,o}$, and effective vaporization rate constant K' as functions of pressure for phenyl azide.

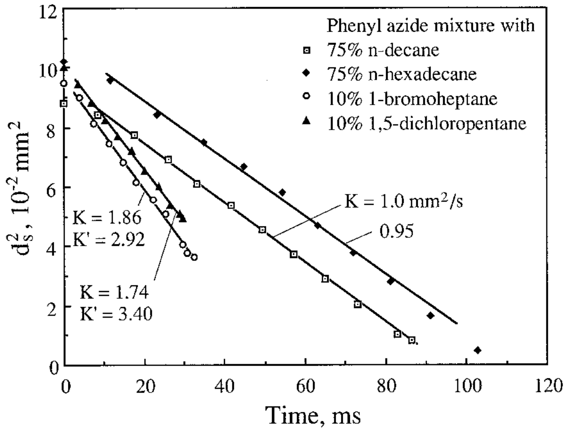

Fig. 11 d^2-law plots for the droplet burning of binary mixtures of phenyl azide with n-decane, n-hexadecane, 1-bromoheptane, and 1,5-dichloropentane.

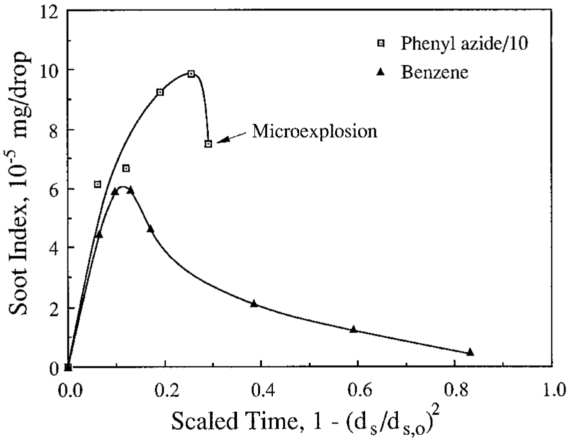

Fig. 12 Variation of the soot index as a function of scaled time for benzene and phenyl azide.

are around 1 mm^2/s, which are slightly higher than that of conventional alkanes. For mixtures of 90% phenyl azide with 10% bromoheptane and dichloropentane, the burning rate constants are around 1.8 mm^2/s, which are slightly lower than that of pure phenyl azide.

Previous experiments[2] have shown that with a small addition of dihalide, e.g., 5% by volume, the gasification rate of the diazide is either unchanged or mildly increased, but the droplet microexplosion event is significantly advanced. Present results show the same behavior of microexplosion with 10% dihalide additives. This shortens the total droplet lifetime and yields a fast overall burning rate, as indicated by the large values of K' in Fig. 11. Thus, mixtures of phenyl azide and dihalides hold potential as fuel additives for enhanced burning. Furthermore, because a large range of the burning rate variation can be achieved by blending phenyl azide with either conventional alkanes or halides, it is reasonable to suggest that fuels and combustors can be developed with specified burning rates by manipulating the extent of blending.

The combustion of phenyl azide, however, is accompanied by an excessive amount of sooting. This is demonstrated in Fig. 12, in which the sooting indices of benzene and phenyl azide are compared. It is seen that the extent of soot emission from burning phenyl azide is an order of magnitude higher than that of benzene. Recognizing that soot emission from benzene itself is higher than that of JP-10 by a factor of 5 or so, the potential use of phenyl azide, in spite of its enhanced burning rate and microexplosion characteristics, may well be limited by its profuse sooting tendency. The chemical mechanism responsible for such an elevated level of soot formation, when the molecular structure of benzene is modified by substitution of a single N_3 group, is however not identified.

Soot Formation in Carborane Burning

Two different samples of carborane of proprietary structure were supplied and tested. Experimentally, it was observed that the extent of soot formation during the droplet burning of these fuels is so excessive that a soot shell was rapidly developed around the droplet, encapsulating it and consequently terminating the combustion. Figure 13 shows the instantaneous images of a burning droplet with the progressive development of the soot shell until complete encapsulation occurs. Figure 14 shows collected samples of the soot shell containing the unburned liquid carborane; note that the elongated tail is caused by the droplet motion, which sweeps some of the soot in the leeward direction of its motion, and that the dimension of the soot shell is typically twice that of the droplet. These results cast doubt on the suitability of carboranes for use as jet fuel unless the sooting issue is satisfactorily resolved.

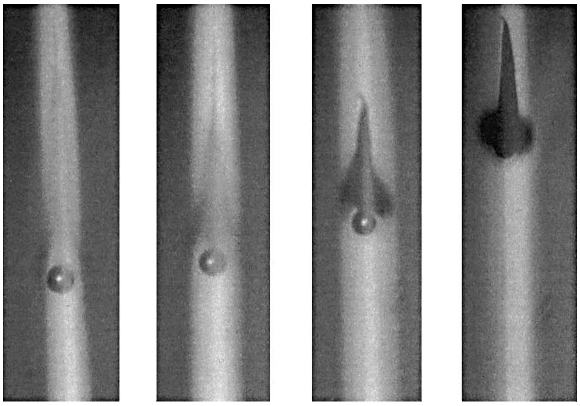

Fig. 13 Photographic sequence showing encapsulation of a burning carborane droplet by the soot shell formed around it.

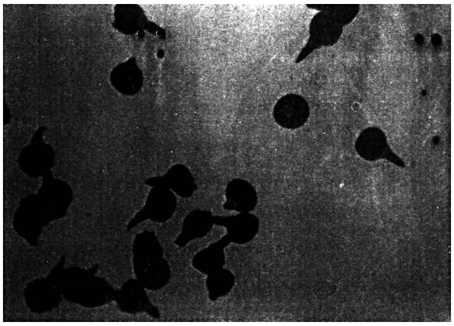

Fig. 14 Collected samples of the soot shells encapsulating the carborane droplets.

Concluding Remarks

In the present investigation, we have experimentally studied the burning characteristics of four newly synthesized energetic propellants. We have demonstrated that the solid 1,4-dimethyl ester cubane is slightly soluble in conventional hydrocarbons and, hence, can be utilized as a jet fuel additive, and that it has the additional attribute of facilitating droplet microexplosion, thereby enhancing the droplet gasification rate when it becomes saturated and condenses out of the solution. For the three liquid fuels dihydrobenzvalene, phenyl azide, and carborane, we have shown that they all soot profusely, with the sooting propensity of phenyl azide being higher than that of dihydrobenzvalene by an order of magnitude, with the sooting propensity of dihydrobenzvalene being higher than that of JP-10 by a factor of 5, and with carborane being so sooty that droplet burning is self-extinguished through the formation of a soot shell around the droplet. As such, although these materials possess high-energy densities, and phenyl azide in particular also exhibits faster gasification rates and an advanced state of microexplosion, it is not at all certain that these materials are suitable as jet fuels without further modification of either the fuel structure or the fuel preparation processes, such as improved mixing to promote premixed burning. The difficulty here is that the requirement of high carbon-to-hydrogen ratios for fuels to have high-energy density is precisely the leading criterion favoring soot formation. As a corollary of this result, it is also emphasized that (high) energy density does not automatically imply fast burning rates, and that it is also not the only criterion in the formulation of a high-performance propellant. Indeed, in the process of either modifying an existing propellant or formulating a new propellant, it is critical to ensure that the established desirable propellant combustion characteristics, including the sooting propensity, not be compromised.

Acknowledgment

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