

PRESSURE EFFECTS IN DROPLET COMBUSTION OF MISCIBLE BINARY FUELS

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Introduction

The objective of this research is to improve understanding of the combustion of binary fuel mixtures in the vicinity of the critical point. Fiber-supported droplets of mixtures of n-heptane and n-hexadecane, initially 1 mm in diameter, were burned in room-temperature air at pressures from 1 MPa to 6 MPa under free-fall microgravity conditions. For most mixtures the total burning time was observed to achieve a minimum value at pressures well above the critical pressure of either of the pure fuels. This behavior is explained in terms of critical mixing conditions of a ternary system consisting of the two fuels and nitrogen. The importance of inert-gas dissolution in the liquid fuel near the critical point is thereby re-emphasized, and nonmonotonic dependence of dissolution on initial fuel composition is demonstrated. The results provide information that can be used to estimate high-pressure burning rates of fuel mixtures.

Although near-critical conditions occur in many practical applications of droplet combustion, understanding of high-pressure combustion of fuel mixtures is incomplete. For normal pressures, well below critical values, both experimental and theoretical work on the combustion of droplets of miscible binary fuels have confirmed and explained three-stage (normal -slow-normal) burning and the occurrence of disruption under suitable conditions. The few experimental studies that have been performed on binary fuel mixtures at elevated pressures (ref. 1, 2) concerned n-heptane, n-hexadecane mixtures and showed that three-stage droplet burning persists, at least up to 3 MPa, but becomes less pronounced with increasing pressure. On the other hand, a computational study of the evaporation of an n-heptane, n-octane mixture in hot nitrogen showed no staged evaporation but attainment of critical mixing above 6 MPa (ref. 3). There is considerable knowledge about the high-pressure combustion of pure-fuel droplets, including both experimental (ref. 4-9) and theoretical (ref. 5, 6, 10-16) work. This research established the subcritical decrease in burning lifetime with increasing pressure, mainly through the decreasing diffusion coefficient, leading to a minimum burning lifetime at a pressure in the vicinity of the critical value. The value of this minimum lifetime and the pressure at which it occurs are affected strongly by the high solubility of inert gases in the liquid fuel near the critical point (ref. 3, 5, 12-14, 16). Critical conditions are modified by this absorption, so that phase interfaces with latent heats can exist at pressures well above the critical pressure of the pure fuel. In a binary mixture of fuel and inert gas, at any given pressure there is a critical mixing point, at which the gaseous and liquid phases become identical, having a temperature above which the system maintains a single phase. During the burning

or evaporation of a pure fuel droplet, at successively higher pressures, the liquid-gas interface eventually reaches a critical mixing point; at and beyond this critical mixing, phase distinctions and latent heats vanish. The minimum burning lifetime occurs at a pressure near those for which critical mixing is achieved at some time during the droplet combustion history.

The present study addresses high-pressure combustion of binary-fuel droplets, necessitating consideration of ternary mixture diagrams to explain the influence of inert-gas absorption on attainment of critical mixing. Advantage is taken of microgravity facilities to enable burning lifetimes to be measured up to 6 MPa without influences of natural convection and without loss of the ability of a fiber to suspend the droplet. Minima of burning lifetimes are measured, and the pressures at which those minima occur are identified. The experimental results are explained by considerations of critical mixing. Staged burning, although weak, is not entirely inconsequential in explaining certain aspects of the minima. The behavior of the particular alkane mixture studied should be representative of that of other binary alkane mixtures and of many other binary fuel mixtures as well.

Experimental Apparatus and Procedure

The combustion experiments were performed in microgravity in a drop tower at the NASA Lewis Research Center that provides 2.2 seconds of microgravity (less than 10^{-5} times normal gravity), so that the buoyancy effects could be negligible. The suspended droplet technique was used, which is good enough to reveal pressure effects on burning lifetime of the binary fuel droplets. The experimental apparatus and procedure in the present study are basically the same as in the previous study by the authors (ref. 2). The initial droplet diameter d_0 was approximately 1 mm. All the burning times were corrected to that of the droplet with $d_0 = 1$ mm by assuming d^2 -law for the burning time. The corrected burning time is called burning lifetime in the present paper. The fuels were n-heptane and n-hexadecane mixtures with initial hexadecane mass fraction Y_0 (or initial hexadecane mole fraction (X_0)), ranging from 0 (pure heptane) to 1.0 (pure hexadecane). The ambient gas used was air at pressures ranging from 1.0 to 6.0 MPa, which exceeds the critical pressure of either of pure heptane (2.74 MPa) and hexadecane (1.41 MPa).

Results

Figure 1 exhibits the measured burning lifetimes t_b as functions of pressure P for five different initial hexadecane mass fractions Y_0 . No experiment was performed at $P = 6$ MPa for $Y_0 = 0.63$, but a corresponding set of experiments that include this point was performed for pairs of droplets separated by 4 mm. The burning lifetimes for the droplet pairs were longer by amounts ranging from about 0.3 at 1 MPa to about 0.1 at 6 MPa (as expected from effects of droplet interactions without natural convection), but otherwise they exhibited the same trends seen in Fig. 2. The point in parentheses in Fig. 1 was obtained from the droplet-pair data by applying the 0.1 s correction for interaction.

Figure 1 shows that the minimum of t_b occurs at about $P = 3$ MPa for both pure fuels and at higher pressures for the mixtures. The dependence of the pressure P_m at which t_b is a minimum on the initial hexadecane mole fraction in the liquid phase X_0 is plotted in Fig. 2. The initial hexadecane mole fraction X_0 is used as the abscissa instead of the mass fraction Y_0 because the dependence shown in this figure is largely influenced by the phase equilibrium as will be discussed later, in which the mole fractions of the phase interface play an important role. It is seen that adding a small amount of hexadecane to pure heptane causes P_m to increase sharply. The value of P_m soon reaches a maximum, and further addition of hexadecane causes P_m to decrease gradually.

Discussion of Binary Systems

Figure 3 shows diagrams of phase equilibrium for three two-component systems, (a) n-heptane/nitrogen, (b) n-hexadecane/nitrogen and (c) n-heptane/n-hexadecane. These diagrams have been calculated by equating the fugacities of each component in each phase, by the method shown in Reid et al. (ref. 17), using the Peng-Robinson equation of state. The data needed for these calculations are available in Reid et al. (Ref. 17). Nitrogen is selected here as representative of the inerts (principally N_2 , CO_2 and H_2O) present during combustion because of lack of data for other species. This seems reasonable because the polar nature of H_2O

is not likely to be very significant at the relatively high temperatures of interest here (ref. 5). The solid lines in Fig. 3 are liquid compositions and the dashed lines gas compositions; they meet at the critical mixing point.

The qualitative characteristics seen in Figs 3a and 3b are quite similar. At normal atmospheric pressure, the mole fraction of nitrogen absorbed in the liquid is very small, but it becomes appreciable near the critical pressure of the pure fuel and is responsible for the emergence of the critical mixing point above that pressure. At any given time during the combustion of a droplet of a pure fuel, the thermodynamic states will lie along a locus in Fig. 3a or 3b, going from the left-hand edge and the flame temperature at the flame sheet to the right-hand edge and the droplet temperature at the center of the droplet. At normal atmospheric pressure, as the temperature decreases this locus reaches the phase equilibrium curve for the gas at the interface then jumps essentially to the right-hand edge and remains there in the liquid. In the opposite extreme, at sufficiently high pressures, the locus avoids the boundary of the two phase region entirely and moves continuously from the left to the right edge. As the pressure is increased above the normal atmospheric value, the magnitude of the jump in the composition X that occurs at the phase boundary decreases, and that jump finally disappears when the pressure becomes high enough for the locus to meet the phase boundary at the critical mixing point. Depending on the shape of the phase boundary, the locus of states in the liquid may or may not follow that boundary over a nonzero range of temperature for pressures equal to or slightly above those for which the intersection occurs at the critical mixing point. However, eventually the locus must leave the boundary to reach the right edge, and as indicated above, at sufficiently high pressures it does not encounter the boundary at all.

The shape of the locus of states discussed above depends, of course, on values and variations of transport properties, as well as on time during the droplet burning history. For typical initial conditions, as time increases the locus intersection moves towards critical mixing, and it reaches this condition if the pressure is sufficiently high (ref. 3, 13). The pressure P_m is approximately that for which this condition occurs roughly in the middle of the burning history. The differences in the ratios P_m/P_c for heptane and hexadecane are associated with the quantitative differences between Figs. 3a and 3b. The phase boundary temperatures are much lower in Fig. 3a, but the flame and initial droplet temperatures are nearly the same for the two fuels. At 3 MPa the locus of states typically reaches a value of X greater than 0.98 at a temperature around 500 K, and this is sufficient to avoid the phase boundary for heptane. Because of the higher temperatures in Fig. 3b, that avoidance does not occur at 2 MPa but finally does begin to occur around 3 MPa, giving a much larger ratio of P_m/P_c for this fuel. The higher critical temperature for hexadecane (722 K), in comparison with heptane (540 K), is thus the main source of its larger value of P_m/P_c . Another contributing factor is the fact that the heat capacity of hexadecane is larger than that of heptane at the same ratio of temperature to critical temperature, so that more heating is required for hexadecane to reach critical mixing.

This same reasoning explains why P_m/P_c is larger for vaporization (ref. 13) or for burning in nitrogen-enriched atmospheres (ref. 2). Under such situations, the effective flame temperature is lower, and therefore, far from the droplet, the locus of states begins closer to the phase boundary. At lower driving temperatures, higher pressures are needed to reach critical mixing and avoid the two phase region.

The diagram of phase equilibrium for the binary fuel mixtures without inert, shown in fig. 3c, is different from those of Figs. 3a and 3b. A normal phase boundary occurs at atmospheric pressure. These two liquids are sufficiently similar that there are no azeotropes under any conditions. A critical mixing point appears when the pressure is raised above the critical pressure of hexadecane. Above the critical pressure of heptane, a lower critical mixing point occurs as well. The extent of the two-phase region decreases with increasing pressure and eventually disappears at a critical point of the mixture P_{C3} , above 3 MPa. At high pressures the two-phase region has a larger mole fraction of heptane than hexadecane in both phases. These characteristics are relevant to the behavior of the ternary system, as discussed below.

Discussion of the Ternary System

Figure 4 shows calculated diagrams of phase equilibrium for the ternary n-heptane/n-hexadecane/nitrogen system for four different pressure ranges, (a) $P < P_{C1}$, (b) $P_{C1} < P < P_{C2}$, (c) $P_{C2} < P < P_{C3}$ and (d) $P_{C3} < P$. The calculations were performed by equating the fugacities of both phases for all three constituents. The bases

of these three-dimensional diagrams are standard equilateral triangles with pure components at the vertices and binary mixtures along the edges. Solid curves give liquid-phase concentrations and dashed curves gas-phase concentrations. Isothermal lines are shown at successive temperature increments of 50 K, dashed in the gas, solid in the liquid and chained in excluded regions. The locus of states now goes from the nitrogen vertex at flame temperature to the fuel composition on the heptane-hexadecane face.

The low-pressure characteristics seen in Fig. 4a are clear from the low-pressure curves in Fig. 3. Figure 4 shows that, above the critical pressure of hexadecane, a critical mixing line appears, over a limited range of relative concentrations of heptane and hexadecane. As expected from Fig. 3c, Fig. 4c shows that, above the critical pressure of heptane, there are both upper and lower critical mixing lines. Finally, above the maximum critical pressure of the heptane-hexadecane system, a critical mixing line extends throughout the entire range of relative concentrations of heptane and hexadecane, as seen in Fig. 4d. Addition of small amounts of hexadecane to heptane reduces the solubility of nitrogen in the liquid, as can be seen in Fig. 4b, 4c or 4d from the existence of a plane through the nitrogen vertex for which the liquid-phase nitrogen mole fraction is a minimum. Such behavior typically is associated with the existence of both upper and lower critical mixing points in the heptane-hexadecane system, as seen in Fig. 3c.

Consider first systems having relatively large initial hexadecane mole fractions X_0 in the binary fuel mixture. Such systems lie close to the nitrogen-hexadecane face of Fig. 4c, and their behavior will be very much like that discussed for Fig. 3b. As the droplet vaporizes, the ratio of hexadecane to heptane in the liquid phase increases slowly, and the surface concentration approaches that of the nitrogen-hexadecane system more closely. As the pressure is increased, attainment of critical mixing occurs when the previously discussed locus of states in Fig. 4 reaches the critical mixing line. A higher pressure is required to reach this line than is required with pure hexadecane because the solubility of the inert in the liquid mixture is less than in pure hexadecane.

Consider next systems for which the initial hexadecane mole fraction X_0 is small. This condition maximizes influences of staged burning. As combustion proceeds, the ratio of hexadecane to heptane at the droplet surface increases, slowly at first but then rapidly as the slow stage begins. In the third stage, the hexadecane fraction in the liquid at the surface is well above its initial value, and the inert solubility is correspondingly larger. This stage, however, comprises a small fraction of the burning lifetime when X_0 is small. Phenomena can influence t_b appreciably therefore only if they occur during the first stage. During this stage, the increase in the hexadecane concentration initially reduces the inert solubility and substantially increases the temperature along the critical mixing line in Fig. 4 or 4d. Both of these effects cause critical mixing to be more difficult to achieve and correspondingly give rise to the sharp increase in P_m with X_0 at small values of X_0 in Fig. 2. Since the minimum inert solubility occurs when the molar ratio of hexadecane to heptane plus hexadecane is about 0.15, the surface hexadecane buildup during the first stage implies that X_0 should be less than 0.15 at the maximum in Fig. 2. Consistent with this deduction, it is observed to be about 0.005.

Conclusions

Aspects of staged burning have been seen to have some influence on the pressure at which the minimum burning lifetime occurs in high-pressure droplet combustion of miscible binary fuels. It is necessary to consider absorption of inert gases in the liquid fuel to determine properly the pressure at which the minimum occurs. Diagrams of ternary phase equilibria are helpful for this purpose, despite the dearth of needed high-pressure phase-equilibrium data. Improved understanding of the combustion of binary fuel mixtures in the vicinity of critical conditions can be obtained by investigations of this kind.

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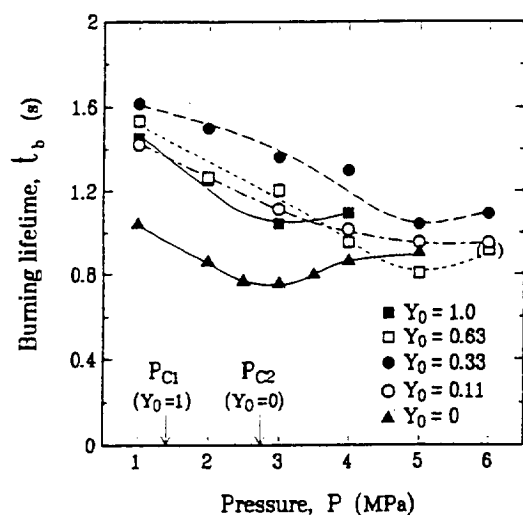


Fig. 1 Dependence of the burning lifetime t_b on pressure P for different initial hexadecane mass fraction in the liquid phase Y_0 .

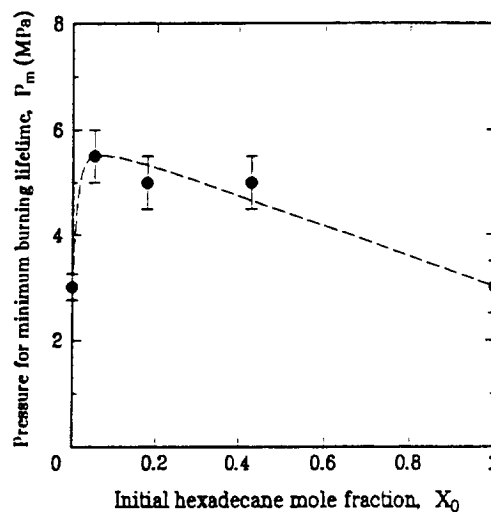


Fig. 2 Dependence of the pressure P_m at which the burning lifetime t_b is a minimum on the initial hexadecane mole fraction in the liquid phase X_0 .

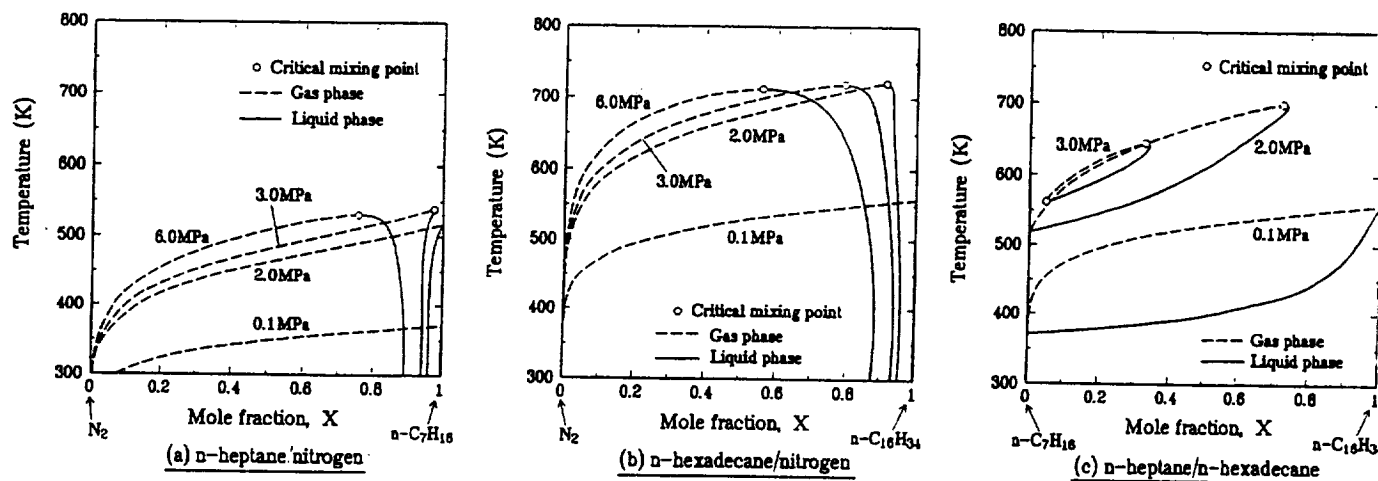


Fig. 3 Calculated diagrams of phase equilibrium for binary systems at different pressures: (a) n-heptane/nitrogen, (b) n-hexadecane/nitrogen, (c) n-heptane/n-hexadecane.

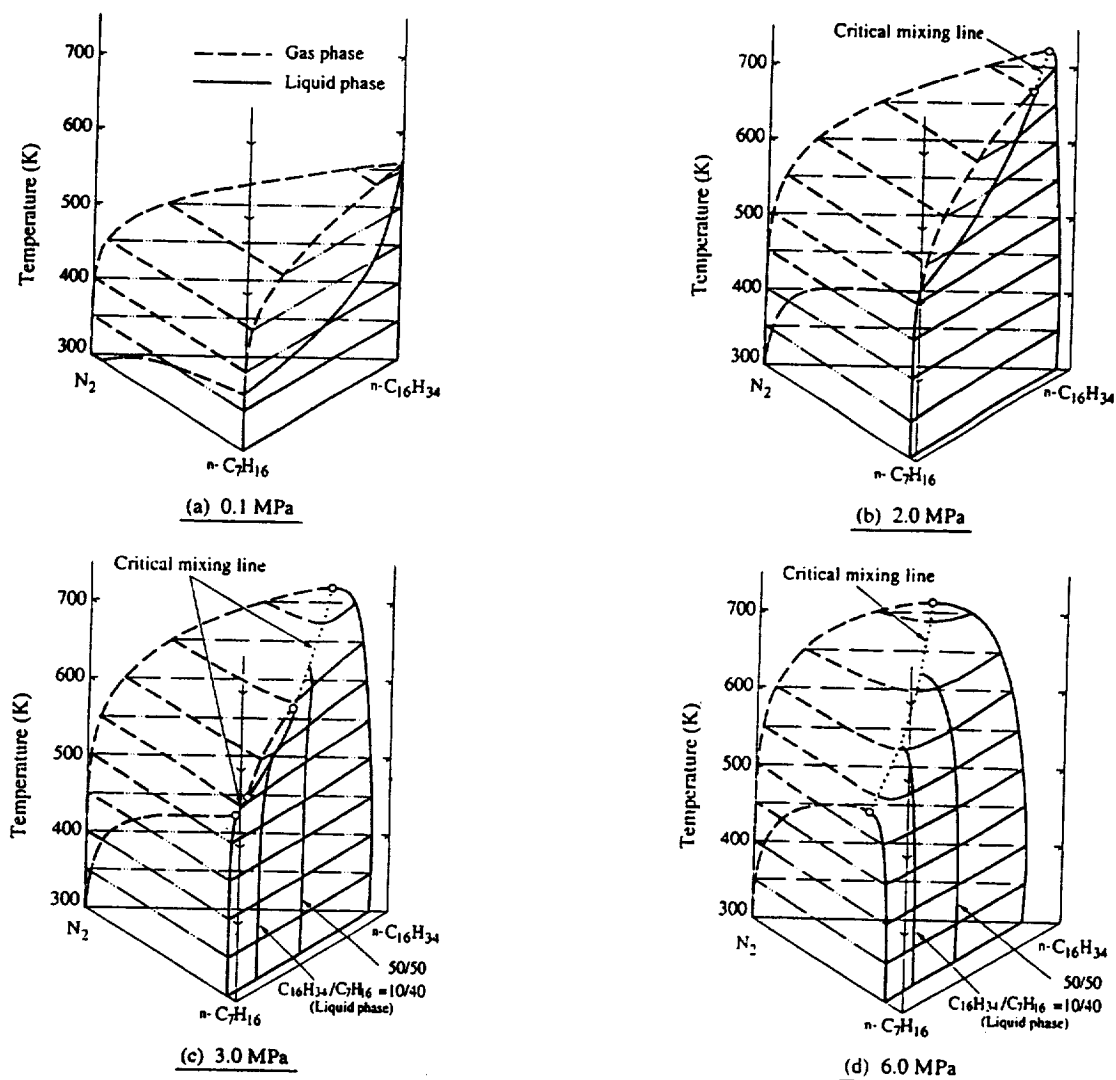


Fig. 4 Calculated diagrams of phase equilibrium for the ternary-heptane/n-hexadecane/nitrogen system; (a) 0.1 MPa ($P < P_{C1}$), (b) 2.0 MPa ($P_{C1} < P < P_{C2}$), (c) 3.0 MPa ($P_{C2} < P < P_{C3}$), (d) 6.0 MPa ($P_{C3} < P$).