The Effect of Liquid Phase Decomposition on the Fuel Droplet Distribution Function

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This paper deals with the problem of coupled evaporation and liquid phase decomposition of hexadecane spray with an assumed one-step second-order reaction. It describes the history of the distribution function $f(D,x,u)$ in a one-dimensional air stream with changing thermochemical properties caused by the evaporation of the fuel spray. Interaction between droplets has been neglected. Ranz-Marshall correlation and Stokes' drag are assumed to describe the evaporation rate and droplet acceleration, respectively, in a flowing medium. Results show that the distribution function changes rapidly due to both decomposition and different individual droplet velocities. Even a small reduction in gas temperature influences the local equivalence ratio and the behavior of the system.

Nomenclature

A = Ranz-Marshall parameter, $= 0.3\, Re_0^{0.5} Pr^{0.3}$
A_I, B_I = constants in the initial distribution function
B = $18\mu_{g0}/\rho_\ell \beta_0$
C = residue concentration/density of pure residue, C_s/C_{s_0}
C_D = drag coefficient
c_p = specific heat of air at constant pressure
C_s = concentration of residue
C_{s_0} = concentration of residue in the pure phase, 0.0032 g mole/cm^3
D = diameter
$\bar{D}_0$ = mean initial diameter of the spray
$\mathfrak{D}$ = $D/\bar{D}_0$
E = activation energy
f = distribution function
F = frequency factor
F_x = drag force in the x direction
Fu = fuel
G = chemical parameter, $(4\bar{D}_0^2 F C_{s_0}/\beta_0)\exp(-E/RT_s)$
h_{fg} = enthalpy of evaporation
m_f = mass of fuel
m_g = total air supplied with the spray which is followed in time (air-to-fuel ratio is assumed to be 15:1, i.e., $m_g = 15m_f$)
Δm_{EV} = net amount of fuel evaporated
Nu = Nusselt number
Pr = Prandtl number
R = gas constant
$\bar{R}$ = diameter reduction rate
Re = Reynolds number
Re_0 = $\rho_{g_0} u_{g_0} \bar{D}_0/\mu_{g_0}$
S = residue
T = local gas temperature
t = time
T_0 = initial gas temperature
T_s = saturation temperature of fuel
u = x component of droplet velocity
u_g = x component of gas velocity
$\bar{u}_g$ = u_g/u_{g0}
x = axial distance from injection point
X = nondimensional distance, $x\beta_0/u_{g0}\bar{D}_0^2$
β = evaporation constant
β_0 = initial evaporation constant
β/β_0 = $(T-T_s)/(T_0-T_s)$
μ_g = gas viscosity coefficient
ξ = u/u_{g0}
ρ = mass density
ρ_ℓ = liquid density
τ = $t\beta_0/\bar{D}_0^2$
ϕ = equivalence ratio

Introduction

THE problem of droplet evaporation has received considerable attention for some time. However, the coupling between evaporation and liquid phase decomposition has not been investigated in detail. Although earlier experimental results[1] can be interpreted on the basis of liquid phase decomposition, this phenomenon was ignored assuming that the typical liquid saturation temperature was too low to cause any liquid phase reaction. While this is generally true at atmospheric pressure, at elevated pressures the corresponding increase in saturation temperature can indeed cause chemical reaction in the liquid phase. Recent studies at the University of Southern California show that even at pressures as low as 4 atm, liquid fuels such as octane, heptane, hexadecane, and others undergo liquid phase decomposition during evaporation.[2] The products of decomposition are heavy tar-like substances which are nonvolatile and slow burning. They appear to be insoluble in liquid fuel and perhaps are formed at numerous sites by nucleation. The chemistry of the residues and the mechanism of their formation are not known at this time.

The overall effect of coupled evaporation and decomposition on a combustor has been investigated using a single droplet in a two-dimensional flowfield with constant thermochemical properties.[3] This analytical study was based upon an assumed second-order, one-step decomposition reaction with several possible frequency factors. The results show that the droplet decomposition can become a serious problem and lead to a substantial reduction in combustion efficiency of a burner. Coupled evaporation and decomposition of fuel spray with a distribution function $f(D,t)$ in a stagnant atmosphere with *constant thermochemical properties* was studied recently with an experimentally determined diameter reduction rate.[4] It was found that when a strong

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Presented as Paper 83-0069 at the AIAA 21st Aerospace Sciences Meeting, Reno, Nev., Jan. 10-13, 1983; received Aug. 15, 1983; revision received March 8, 1984. Copyright © American Institute of Aeronautics and Astronautics, Inc., 1983. All rights reserved.

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coupling existed between evaporation and decomposition very little fuel evaporated and the initial spray of liquid fuel reduced to a distribution of nonvolatile particulate matter. Both of the studies[3,4] referred to here assume constant thermochemical properties of the gas stream. In other words, the changes in gas properties, such as, for example, temperature, density, and viscosity, were neglected in spite of the cooling effect due to the evaporation of the liquid. Other recent investigators[5,6] who have studied only the evaporation of a spray also neglected the changes in gas properties. A review of the current status of droplet evaporation appears in Ref. 7.

The present work deals with the behavior of hexadecane spray undergoing coupled evaporation and liquid phase decomposition in a gas stream with changing thermochemical properties. The gas temperature is assumed to drop due to the evaporation of hexadecane. Thus, the density and viscosity of the gas also change. Significant changes in the history of the distribution function $f(D,x,u)$ are observed analytically when the ambient temperature is affected by droplet evaporation. Because of the decreasing ambient temperature, the rate of change of concentration of the particulate matter decreases.

Analysis

Liquid Phase Decomposition

Figures 1 and 2, reproduced from Ref. 4, show the experimental results indicating liquid phase decomposition of 1-octene and *n*-heptane at higher pressures. At 1 atm pressure the $D^{*2}-\tau$ relationship is linear and the nonlinear behavior is seen only at elevated pressures as shown in the figures. This behavior has been observed for both pure fuels and typical commercial blends. In the absence of a detailed knowledge of the decomposition rate, in the present work, a second-order, one-step reaction[2] with negligible enthalpy of reaction has been assumed.

In this model the fuel decomposes following $2Fu \rightarrow S$ (Fu is fuel and S a nonvolatile, insoluble residue) with an activation energy of 40 kcal/mole. The frequency factor has been varied from $F=10^{15}$ to 10^{20} cm^3/mole-s spanning the range of an extremely weak coupling to a very strong coupling between evaporation and decomposition.

Assumptions

The following assumptions are made for analyzing the problem.

1) Stokes' drag $C_D = 24/Re$ (Re = local Reynolds number based upon droplet diameter) is applicable.

2) Ranz-Marshall correlation $Nu = 2 + 0.6 Re^{0.5} Pr^{0.3}$ describes the evaporation in a flowing medium.

3) The flowfield is steady and one-dimensional, and the initial droplet diameter distribution function is of the form $A_I D^3 \exp(-B_I D^2)$. Initially, at the point of injection, all droplets are assumed to travel at a uniform initial velocity.

4) Liquid temperature is always the saturation temperature corresponding to the ambient pressure.

5) As the liquid evaporates, the gas temperature drop is determined by the latent enthalpy of evaporation of the fuel. No other interaction between the droplets and the gas (air stream) affects the gas temperature.

6) The viscosity coefficient μ_g and density ρ_g are proportional to $\sqrt{T}$ and $1/T$, respectively. Three possible cases for the variation of gas velocity, namely, u_g proportional to T, $\sqrt{T}$, and constant were also investigated. Consistent with the other conservation equations each of these cases will correspond to different specific flow geometries. Since the characterization of the duct is beyond the scope of this study, the behavior of the flowfield for these three cases was studied without considering the system geometry. The evaporation constant β is assumed to be proportional to the difference in temperature between the ambient and saturation temperatures of the liquid. The ambient pressure is constant and hence the saturation temperature of the liquid is also a constant.

Governing Equations

Ignoring interparticular collision the conservation of number for a distribution $f(D,x,u)$ in a substantial derivative form[8] is given by

$$\frac{\mathrm{d}f}{\mathrm{d}t} = -f\left(\frac{\partial F_x}{\partial u} + \frac{\partial u}{\partial x} + \frac{\partial \bar{R}}{\partial D}\right) \tag{1}$$

The first term on the right-hand side depends upon the choice of the drag force. The second term can be evaluated from the momentum equation of the one-dimensional flowfield and the third term can be determined from the model of diameter reduction rate involving the evaporation constant and Ranz-Marshall correlation equation. Droplet shattering, collision, and coalescence have been neglected in Eq. (1).

Using nondimensional variables $\xi = u/u_g$; $\tau = t\beta_0/\bar{D}_0^2$ ($\bar{D}_0$ = initial mean diameter of the spray); $\mathfrak{D} = D/\bar{D}_0$; $X = x\beta_0/\bar{D}_0^2 u_{g_0}$ and identifying the initial values with a subscript 0, Eq. (1) takes the form of Eq. (2) and the remainder of the governing equations is as follows:

Conservation of number:

$$\frac{\mathrm{d}f}{\mathrm{d}\tau} = -\frac{f}{\mathfrak{D}^2}\left[B\sqrt{\frac{T}{T_0}}\,\frac{\bar{u}_g - 2\xi}{\xi} + 0.5\frac{T/T_0 - T_s/T_0}{1 - T_s/T_0}\right.$$
$$\left.\times\left\{1 + 0.5A\left(\frac{T_0}{T}\right)^{0.75}\sqrt{(\bar{u}_g - \xi)\mathfrak{D}}\right\}\right] \tag{2}$$

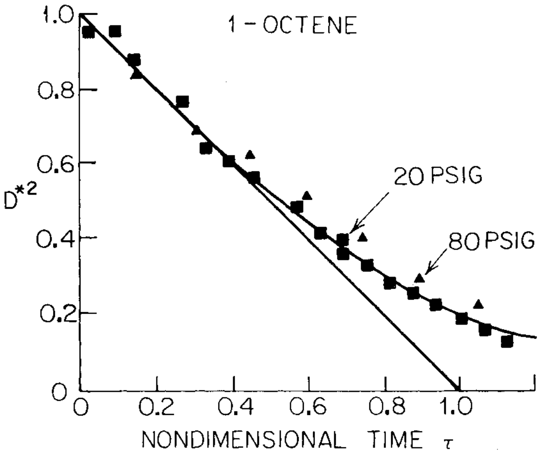

Fig. 1 Evaporation of a 3.5-mm 1-octene droplet suspended over a 450°C plate at two different pressures. $D^* = D/D_0$.

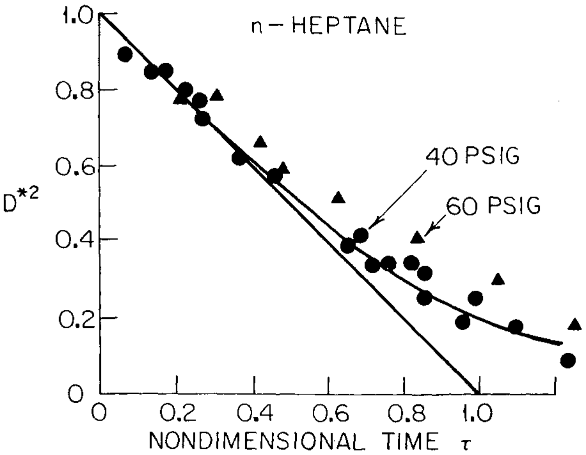

Fig. 2 Evaporation of a 2.4-mm n-heptane droplet suspended over a 450°C plate at two different pressures. $D^* = D/D_0$.

Momentum equation:

$$\frac{\mathrm{d}\xi}{\mathrm{d}\tau}=\frac{B}{\mathfrak{D}^2}\sqrt{\frac{T}{T_0}}\,(\bar{u}_g-\xi) \tag{3}$$

Diameter reduction rate:

$$\frac{\mathrm{d}\mathfrak{D}}{\mathrm{d}\tau}=-\frac{0.5}{\mathfrak{D}}\,\frac{T/T_0-T_s/T_0}{1-T_s/T_0}\left[1+A\left(\frac{T_0}{T}\right)^{0.75}\times\{(\bar{u}_g-\xi)\mathfrak{D}\}^{0.5}\right] \tag{4}$$

Rate of change of residue concentration^2:

$$\frac{\mathrm{d}C}{\mathrm{d}\tau}=G(1-C)^2-\frac{3C}{\mathfrak{D}}\left(\frac{\mathrm{d}\mathfrak{D}}{\mathrm{d}\tau}\right) \tag{5}$$

Ambient temperature:

$$T/T_0=1-(h_{fg}\Delta m_{EV}/c_pT_0m_g) \tag{6}$$

Droplet location:

$$\frac{\mathrm{d}X}{\mathrm{d}\tau}=\xi \tag{7}$$

The system of equations includes the assumed dependence of μ_g, ρ_g, and β on the local gas temperature. Ranz-Marshall correlation and the evaporation constant β are used in Eq. (4) to include the combined effect of the flowfield and the local temperature change on the diameter reduction rate. The local temperature affects β, μ_g, ρ_g, and u_g. Thus, the ratio of the local gas temperature to the initial gas temperature appears in Eqs. (2-4).

The concentration of residue species changes, first of all, due to the formation of residue as a result of liquid phase decomposition. Evaporation of liquid fuel reduces the volume of the droplet which, in turn, causes an increase in residue concentration (mass of residue/volume). Equation (5) includes both of these phenomena and describes the combined effect of decomposition and evaporation on the rate of change of residue concentration. Magnitudes of each of the two terms of Eq. (5) describe the relative importance of decomposition rate over the evaporation rate in a given system.

Equations (2-7), a total of six equations, have six unknowns: f, ξ, $\mathfrak{D}$, C, T, and X. They are solved using a fourth-order Runge-Kutta method with the following initial conditions:

$$\text{At } \tau=0;\ f=A_1D^3\exp(-B_1D^2);\ A_1=\frac{81}{128}\frac{\pi}{\bar{D}_0^3};\ B_1=\frac{9\pi}{16\bar{D}_0^2}$$

$$\xi=0.2,\quad C=0,\quad T_0=800\,\mathrm{K},\quad u_{g_0}=15\,\mathrm{m/s},\quad \bar{D}_0=50\,\mu\mathrm{m}$$

The ambient pressure was assumed to be 4 atm with a corresponding fuel saturation temperature of roughly 640 K for hexadecane. A value of $3.5\times10^{-3}\mathrm{cm}^2/\mathrm{s}$ was chosen for the initial evaporation constant β_0. The frequency factor F in the chemical parameter G of Eq. (5) was varied between 10^{15} and $10^{20}\mathrm{cm}^3$/mole-s in order to compare the results for various degrees of coupling between evaporation and decomposition. In the case of a strong coupling, the entire spray becomes a distribution of residue particles soon after injection. On the other hand, a weak coupling is characterized by mostly evaporation and very little decomposition during the lifetime of a spray. Since at this time the decomposition chemistry is not known, it is practically impossible to predict the type of coupling one can expect. However, a large range of F values is chosen to study the behavior of the system under

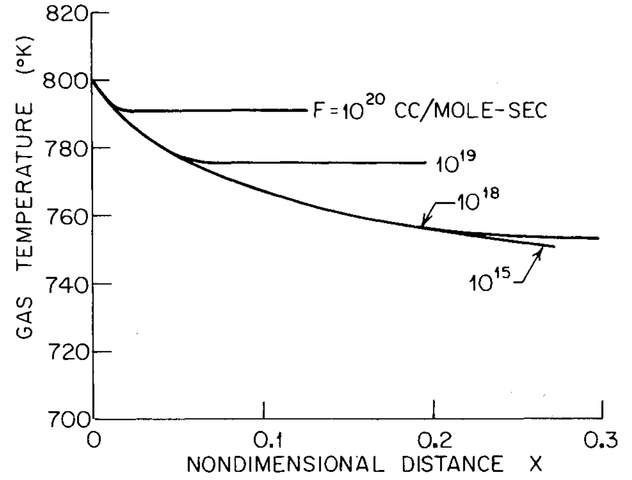

Fig. 3 Effects of various frequency factors on the ambient temperature distribution.

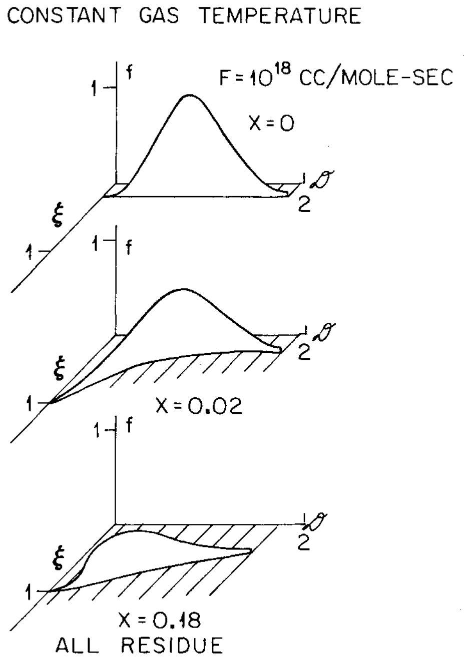

Fig. 4 Behavior of distribution function for constant ambient temperature.

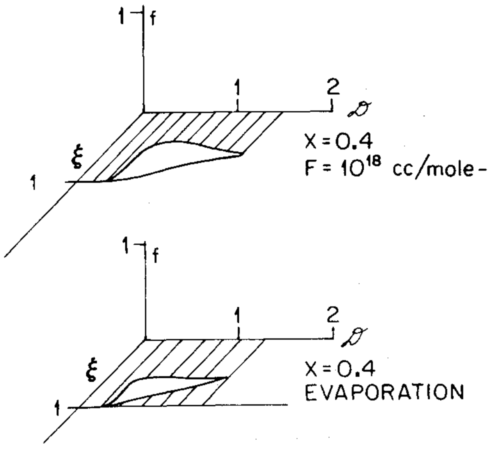

Fig. 5 Comparison of distribution functions for only evaporation and only nonvolatile residue particles at $X=0.4$. Constant ambient temperature.

extreme conditions and to focus attention on the importance of droplet decomposition in a high-pressure system particularly where the ambient temperature is affected by evaporation.

Results and Discussion

The solution of Eqs. (2-7) gives the history of the spray as a function of time. Since the spray consists of droplets of different diameters traveling at different velocities, the initial group of droplets will be distributed over different locations at a given time. It is more useful to know the size distribution and the distribution of velocities at a *given location* rather than at a given time. Therefore, new solutions are generated from the old solutions to give $f(\mathfrak{D},X,\xi)$, $T(X)$, $\beta(X)$, and $\phi(X)$ (ϕ = equivalence ratio).

Calculations shown in all of the figures that follow assume u_g to be proportional to the local ambient gas temperature T. No qualitative and only a small quantitative difference in f and ϕ distributions were observed for other variations of u_g. The reason for such a small sensitivity to u_g becomes clear as one examines the temperature distributions shown in Fig. 3. Even for the worst case considered, the temperature drop is only about 6% causing a similar degree of decrease in the ambient gas velocity.

Figure 4 shows the distribution function $f(\mathfrak{D},X,\xi)$ at different locations when the ambient temperature is assumed to be a constant. The distribution function undergoes a rapid "distortion" and the droplet diameters eventually remain unchanged when all of the fuel decomposes into residue particles. Such a situation occurs at $X=0.18$ when a moderate degree of coupling between decomposition and evaporation is assumed ($F=10^{18}$ cm^3/mole-s). Figure 5 shows the distribution function for $X=0.4$, a location far beyond $X=0.18$ where the spray consists only of nonvolatile residue particles. Although the particle diameters do not undergo any change beyond $X=0.18$, the distribution function changes as a result of the changes in particle velocities and X. Figure 5 also compares the case where the spray only evaporates and does not undergo any liquid phase decomposition. The continued reduction in diameter due to evaporation is evident in this case. Both Figs. 4 and 5 represent cases for constant ambient gas temperature. For a variable gas temperature, Fig. 6 shows a definite delay in the formation of residue particles. This delay is caused by a decrease in the evaporation rate due to a gradual reduction of the ambient temperature [Eq. (5)]. The distribution functions shown in Figs. 4-6 are qualitatively similar but differ in details. Unfortunately, however, because of the nature of the isometric plots, many of the detailed differences between the cases are not quite evident. The overall effects of these differences are shown clearly in Figs. 3,7, and 8.

For the case of the variable ambient temperature, evaporation continues until $X=0.24$ is reached when only the residue particles remain in the spray. Thus, the realistic case of gradually decreasing ambient temperature *delays* the formation of residue particles at smaller distances from the injection point. Figure 9 shows the variation of the evaporation constant β along the flowfield for $F=10^{18}$. The enthalpy of evaporation of hexadecane is rather small, and consequently, the net reduction in temperature of the ambient air stream with a mass ratio of 15:1 is also small. Since β depends upon the difference between the ambient and saturation temperatures of the fuel, Fig. 9 shows nearly a 30% reduction in the value of β when the air temperature decreases by nearly 6%. The value of β remains constant beyond $X=0.24$ because beyond this point no liquid remains in the spray. Figure 7 compares the values of the local equivalence ratio for both the variable and constant ambient temperature cases. Because of the reduction in β, the mixture is leaner when the ambient temperature is allowed to change. Ultimately the equivalence ratio for the case of variable

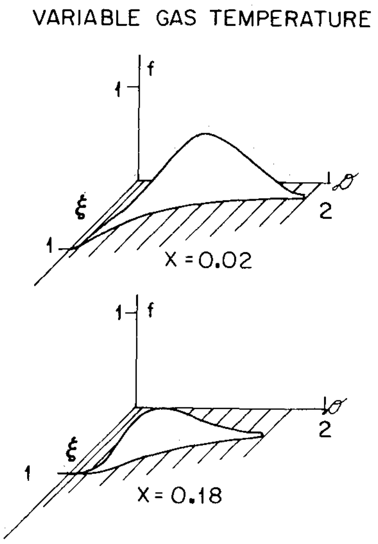

Fig. 6 Distribution function in changing ambient temperature. $F=10^{18}$ cm^3/mole-s.

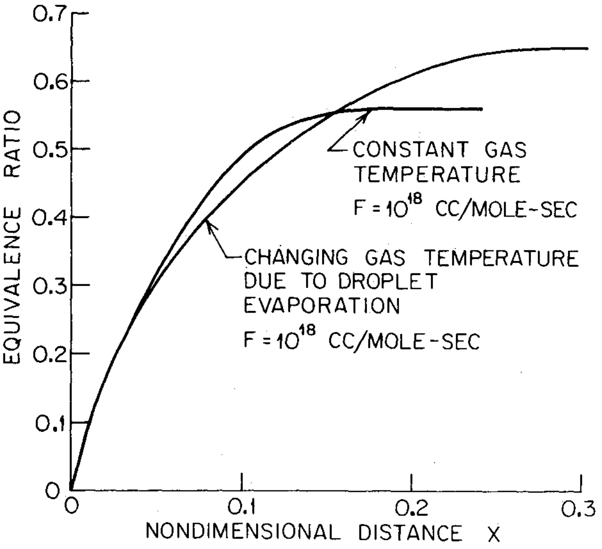

Fig. 7 Local values of equivalence ratio for a constant and variable gas temperature.

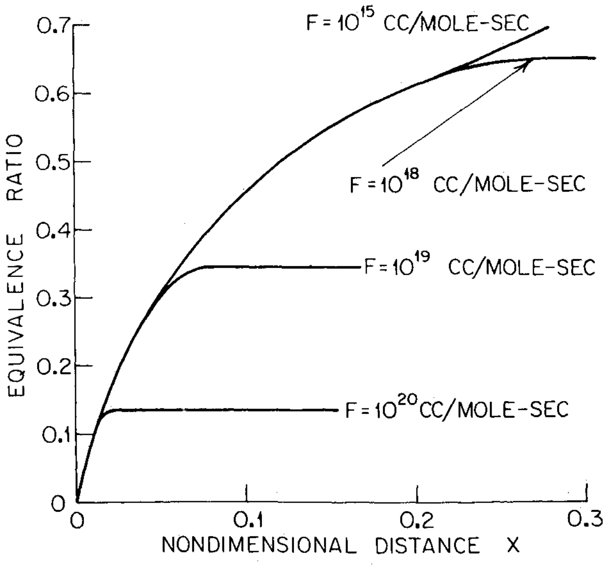

Fig. 8 Effects of various frequency factors on the mixture equivalence ratio.

temperature exceeds that of the constant temperature indicating a marked difference in the system behavior between these two cases. Figure 3 shows that as the decomposition rate increases, significant changes in the temperature distribution of the gas stream are observed.

The corresponding distribution of equivalence ratio for different frequency factors is shown in Fig. 8. If one were to assume that the combustion efficiency is related only to the amount of fuel actually evaporated, then, on the whole, the liquid phase decomposition causes a reduction in the combustion efficiency of a burner. Since the details of the chemical kinetics of decomposition are not known, several frequency factors are chosen to show their effect on the behavior of the system. In addition to the changes in temperature and equivalence ratio, the details of the distribution function changes rapidly with decomposition. Figure 10 is a history of $f(\mathfrak{D},X,\xi)$ at points where all of the liquid has evaporated and only the products of decomposition remain. Cases of weak, moderate, and strong decomposition rates are shown in Fig. 10 to illustrate the differences in the nature of the distribution function with reaction.

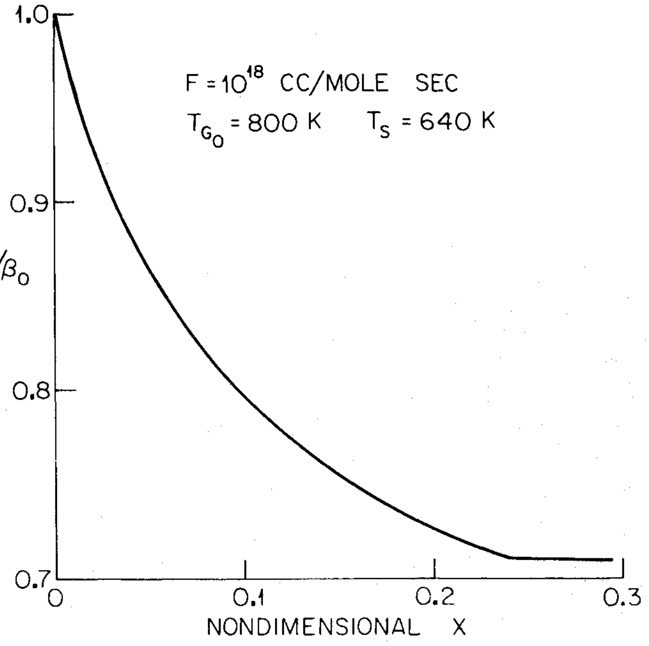

Fig. 9 Reduction of the evaporation constant due to changes in gas temperature.

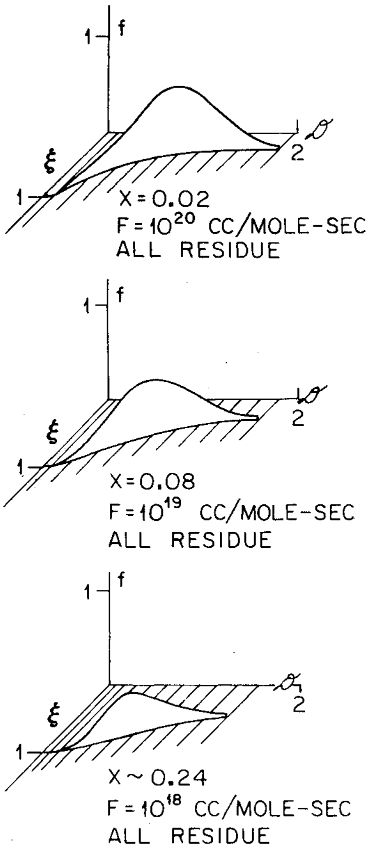

Fig. 10 Remains of the initial spray with all residue species and no liquid.

The present study shows that the changes in the ambient temperature due to evaporation have a strong influence on the system behavior and should not be ignored. A decreasing ambient temperature not only decreases the evaporation rate of the fuel but also delays the buildup of residue concentration in the droplet. On the whole, decomposition of fuel in the liquid phase causes a reduction in the combustion efficiency. It also helps form particulate matter in the exhaust (Fig. 10). In the presence of combustion one can surmise that the residue species would absorb thermal radiation and eventually shatter a droplet loaded with residue. In principle, this situation can offset some of the disadvantages of liquid phase decomposition when the spray is exposed to thermal radiation from the flame in the combustor. Such a case of droplet shattering and possible increase in decomposition rate due to an increase in the temperature of the residue nucleii was not considered in this study.

Experiments show that liquid phase decomposition can be expected in advanced airbreathing propulsion systems operating at high pressures. It is quite possible that diesel engines have similar problems with liquid phase decomposition of the fuel spray. Experimental work on diesel engines is being carried out by the authors to ascertain the results of droplet decomposition in the combustion chamber and its effect on the particulate emission in the exhaust. A more important problem of identifying the chemical nature of the residue and determining a global reaction rate is also being investigated at the University of Southern California.

Acknowledgment

This work was partially supported by AFOSR Grant 82-0222; Dr. B. T. Wolfson was the program manager.

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