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Validity of Droplet Ignition Criteria Derived Assuming Gas-Phase Quasisteadiness

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This work investigates the validity of the droplet ignition criteria that were derived based on the quasi-steady-gas-phase (QSGP) assumption without considering transient fuel vapor accumulation (FVA) effects. Numerical results of the ignition models with transient gas phase and quasisteady gas phase without considering FVA effects are compared with respect to the preignition distribution of fuel vapor concentration, the ignition delay, and the minimum ignitable temperature. Calculations are made for *n*-heptane and *n*-hexadecane, which have very different volatilities, at various ambient temperatures, initial droplet temperatures, and initial droplet diameters. Without considering the transient FVA effects (i.e., ignoring the transient mass conservation equation), the QSGP ignition model considerably underpredicts ignition delays, with errors increasing sharply with increasing fuel volatility. As far as the minimum ignitable gas temperatures are concerned, for both heptane and hexadecane droplets the QSGP results are qualitatively correct, but appear quantitatively underestimated. These results indicate that the existing QSGP droplet ignition criteria derived without considering FVA effects, which have been widely used in droplet and spray ignition analyses, are unsuitable for the determination of ignition delays. They may be used for determining the minimum ignitable temperatures, but significant underestimations may exist.

Nomenclature

A = pre-exponential factor in Arrhenius rate expression
C_p = specific heat at constant pressure
D = effective binary mass diffusivity
d = droplet diameter
E_a = activation energy
H = effective latent heat of vaporization
k = thermal conductivity
L = specific latent heat of vaporization
Le = Lewis number
M = molecular weight
$\hat{m}$ = nondimensional evaporation rate
P = pressure
P_c = critical pressure
Q = specific heat of combustion
R_s = droplet radius
R_u = universal gas constant
R' = gas constant
T = gas-phase temperature
T_a = activation temperature
T_c = critical temperature
T_g = gas temperature
T_m = maximum gas temperature
T_r = reduced temperature
t = time
t_{ig} = ignition delay time
u = gas velocity
Y = species mass fraction
α = thermal diffusivity
Δ = system Damköhler number in the QSGP ignition theory
Δ_I = ignition Damköhler number in the QSGP ignition theory
θ = liquid-phase temperature
ν = stoichiometric constant
ρ = density
$\dot{\omega}$ = reaction rate

Subscripts

f = fuel
l = liquid
o = oxidant
s = droplet surface
0 = initial
∞ = ambient

Introduction

THE combustion of liquid fuel sprays is responsible for a major portion of the total energy requirements of the world. Clear knowledge of the ignition and combustion processes of fuel droplets is essential for understanding the fundamentals of combustion phenomena as well as for the effective design of practical combustion systems. The assumption of gas-phase quasisteadiness has conventionally and successfully been employed to simplify droplet ignition and combustion analyses. This assumption was based on the argument that, owing to significant density disparity between liquid and gas, the properties at the droplet surface change at rates much slower than those of the gas-phase transport process. During the characteristic gas-phase diffusion time the droplet surface location and thermodynamic conditions can be considered to be constant, and the gas-phase processes can thus be treated mathematically as steady. Law et al.[1] further showed that the transient initial droplet evaporation process can still be treated assuming gas-phase quasisteadiness as long as the mass conservation of the fuel vapor in the gas phase is properly accounted for. The transient gas-phase transport process, which can still be treated using simplified quasisteady energy and species equations, together with transient mass conservation equation, has been called fuel vapor accumulation (FVA).[1]

Without considering FVA effects (i.e., ignoring the transient mass conservation equation), Law applied the quasi-

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steady-gas-phase (QSGP) assumption to droplet ignition analysis in 1975.[2] Using the matched asymptotic technique in the limit of large activation energy, an ignition criterion in terms of ignition Damköhler numbers was derived analytically. Law then developed a thermal droplet ignition theory[3] for calculating ignition delay times based on this ignition criterion, with the transient droplet heating approximately treated using the distillation model.[4] Subsequently, Mawid and Aggarwal[5] modified Law's ignition theory with the nonunity exponent chemical kinetics suggested by Westbrook and Dryer.[6] Li and Renksizbulut[7] further extended the work of Law[2,3] and Mawid and Aggarwal[5] to include the effects of variable thermophysical properties and nonunity Lewis number. Law and Chung[8] also extended the application of the ignition criterion to droplet ignition problems in a spray environment by including ambient fuel vapor effects. Makino[9] expressed the previous criteria in more convenient explicit forms. Since the ignition criteria can be conveniently applied for determining whether and when a droplet ignites, the QSGP ignition criteria of Law[2] and Mawid and Aggarwal[5] have been widely employed in droplet and spray combustion analyses.[10,11] However, the validity of such criteria has not been carefully tested.

The objective of this work is to investigate the validity of the existing droplet ignition criteria, which were derived based on the QSGP assumption without considering the transient FVA effects. Such criteria have been widely applied in spray combustion analyses. For various fuel volatilities, initial droplet temperatures, ambient gas temperatures, and droplet diameters, we compare the numerical results of a QSGP ignition model[5] and a fully transient ignition model[13,14] with respect to preignition fuel vapor concentration, ignition delay time, and the minimum ignitable temperature. Experimental ignition data will also be compared with model calculations.

Theoretical Work

QSGP ignition model follows Mawid and Aggarwal,[5] who modified Law's work with nonunity exponent chemical kinetics. According to the QSGP ignition theory of Law,[2,3] a droplet of given properties vaporizing in an environment achieves ignition if the system Damköhler number Δ exceeds the ignition Damköhler number Δ_I, i.e.,

$$\Delta \geq \Delta_I(\beta) \tag{1}$$

For nonunity-exponent kinetics, according to Mawid and Aggarwal[5]:

$$\Delta = \left[\frac{A(M_f)^{1-a_f}}{\rho_\infty D_\infty (M_o)^{a_o}}\left(\frac{PC_p}{R'Q}\right)^{a_o+a_f}\right]\left[\frac{Y_{0\infty}^{a_o}\exp(-T_a/T_\infty)(\hat{m}R_s)^2}{\left(\frac{C_pT_\infty}{Q}\right)^{a_o+a_f}\left(\frac{C_pT_\infty^2}{T_aQ}\right)^{3-a_f}}\right] \tag{2}$$

With $a_f = 0.25$, $a_o = 1.5$, according to Makino,[9]

$$\Delta_I = \frac{1}{2\Gamma(1.25)}\left[\frac{4}{e(1-\beta)}\right]^4 - 0.68\left[\frac{4}{e(1-\beta)}\right] \tag{3}$$

where $\Gamma(1.25) = 0.90640$. The nondimensional parameters appearing in Eqs. (2) and (3) are defined as

$$\hat{m} = \ln(\beta/\hat{H}), \qquad \beta = \hat{T}_\infty - \hat{T}_s + \hat{H}$$
$$\hat{T} = C_pT/Q, \qquad \hat{H} = H/Q$$

The quantities of $\hat{m}$, $\hat{T}_s$, and R_s required in Eqs. (2) and (3) are obtained from liquid-phase solutions.

The transient ignition model, generally following Niioka et al.,[13] is described in the Appendices.

Table 1 Properties of fuel/air mixtures used in computation[a]

	n-heptane	*n*-hexadecane
C_p, cal/g K	0.261	0.267
C_{pl}, cal/g K	0.532	0.532
k, cal/cm s K	12.95×10^{-5}	14.57×10^{-5}
k_l, cal/cm s K	30.85×10^{-5}	36.42×10^{-5}
ρ, g/cm^3	4.72×10^{-4}	4.04×10^{-4}
ρ_l, g/cm^3	0.683	0.773
L, cal/g	87.5	86.2

[a]The values of gas-phase properties presently listed were estimated using the ⅓-rule based on an ambient gas temperature of 1500 K and the fuel boiling point. However, actual value of ambient gas temperature was used for determining gas-phase properties in calculations. The liquid-phase properties were based on the initial droplet temperature.

The conduction-limit analysis is adopted for the liquid phase in both models.

As far as the ignition criterion is concerned, Mawid and Aggarwal, following Law, used the initiation of a gas-phase temperature maximum, whereas Niioka et al. used the appearance of the first inflection point in the $T_m - t$ curve (i.e., $d^2T_m/dt^2 = 0$), which represents the thermal runaway condition and is physically more rigorous, as the ignition criterion. The difference in the ignition criteria adopted in the two models makes it inappropriate to compare the results of the two models directly. For direct comparison of the transient and QSGP results to be possible, the appearance of $T_m = T_\infty + 0.1$ K will be used equivalently as the initiation of a gas-phase temperature maximum.

Two paraffin hydrocarbon fuels of different volatilities, *n*-heptane and *n*-hexadecane, are studied. Since the purpose of this study is on the effects of transient gas-phase transport, detailed chemical kinetics will not be adopted. In the one-step Arrhenius reaction rate expression the exponents for oxygen and fuel vapor concentrations are, respectively, $a_o = 1.5$ and $a_f = 0.5$. The activation energies chosen are, respectively, 38 and 35 kcal/mole.[15] The pre-exponential factors, extracted by comparing the transient ignition calculations with Faeth and Olson's[16] experimental data, are, respectively, 1.1×10^{11} and 7×10^{10} in cm-s-mole units for *n*-heptane and *n*-hexadecane.

Thermodynamic properties of the fuels were determined based on Vargaftik[17] or Reid et al.[18] The thermodynamic properties of fuel/air mixtures used in computation are listed in Table 1.

Results and Discussion

General Concept

The droplet ignition theory of Law[2,3] was developed using the distributions

$$\frac{Y_f - Y_{f\infty}}{Y_{fs} - Y_{f\infty}} = \frac{1 - \exp[-(\hat{m}R_s/r)]}{1 - \exp(-\hat{m})} \tag{4}$$

$$\frac{T - T_\infty}{T_s - T_\infty} = \frac{1 - \exp[-(\hat{m}R_s/r)]}{1 - \exp(-\hat{m})} \tag{5}$$

without considering the FVA effects. The QSGP distributions dictated by Eqs. (4) and (5), derived without the constraint of transient mass conservation equation, actually violate the mass conservation law during the early preignition period when the gas phase is essentially transient. This will be shown to lead to underestimated ignition delay times.

Computations are first performed for cases of droplet evaporation in an inert ambient. As far as droplet temperature and droplet evaporation rate are concerned, Fig. 1 shows good agreement between the results of the transient and the QSGP model. This is expected since the reliability of applying the

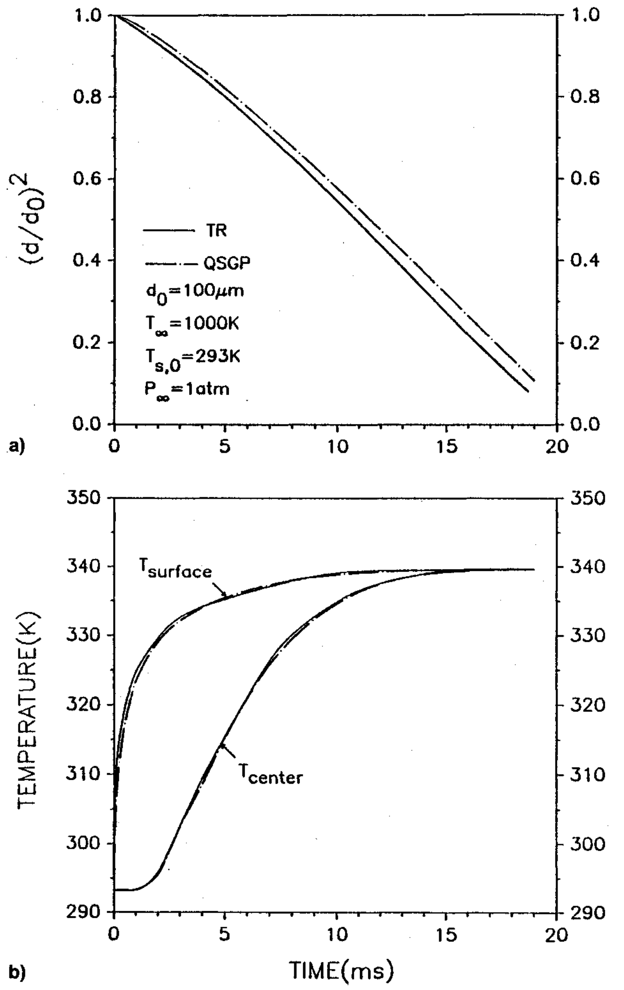

Fig. 1 Comparison of the droplet temperature distributions and the diameter variations calculated by the transient and the QSGP analyses for a droplet vaporizing in an inert ambient: a) $(d/d_0)^2$ and b) droplet temperature.

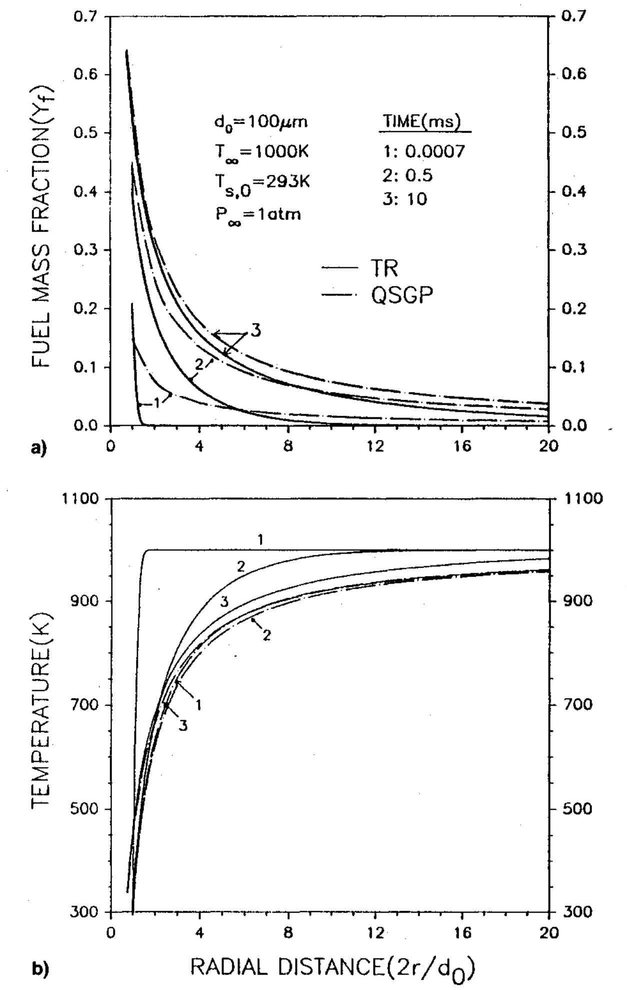

Fig. 2 Comparison of the distributions of fuel vapor concentration and gas temperature calculated by the transient and the QSGP analyses for an *n*-heptane droplet in an inert ambient: a) fuel mass fraction and b) gas temperature.

QSGP assumption to droplet evaporation or burning rate predictions at low pressures has been well recognized. Figure 1 also reveals subtle information that the QSGP assumption leads to slightly underestimated droplet surface temperatures and droplet evaporation rates.

As the gas phase is considered, however, striking differences are manifested. Figures 2 and 3 compare the calculated radial Y_f and T_g distributions at different times, respectively, for a heptane and a hexadecane droplet. The QSGP distributions plotted in Figs. 2 and 3, according to the QSGP droplet evaporation theory without considering the FVA effects, are Eqs. (4) and (5). Significant differences between the transient and QSGP model results exist for the heptane droplet, particularly during the early stage (Fig. 2). The higher QSGP $Y_f - r$ distribution clearly reveals its violation of mass conservation law. It is shown in Fig. 2a that for volatile heptane the fuel vapor concentration at the droplet surface has already attained a relatively high value at the low initial surface temperature $T_{s,o}$ = 293 K. In the QSGP analysis, a radial distribution of Y_f in the gas-phase-steady form expressed by Eq. (4) is obtained, when in reality, the fuel vapor should not have diffused out. Considerable differences still exist at 0.5 ms. Afterwards, the transient Y_f distribution gradually approaches the QSGP one, and at 10 ms the two curves appear closer. Similar situations happen for T_g distributions except that the QSGP distributions are now lower (Fig. 2b). However, the effect of the near-field temperature reduction to the ignition process is not included in the QSGP ignition theory, because in the QSGP theory ignition is considered to occur in the far-field[2] where the gas temperature approaches T_∞. This can be realized by examining the QSGP ignition criterion [Eqs. (1–3)]. The key parameters determining whether $\Delta \geq \Delta_I$ is satisfied for a droplet in a prescribed environment include only T_s (and, hence, Y_s) and T_∞ (letting alone R_s, $Y_{o\infty}$, and other thermophysical constants). It will be shown in Figs. 4a and 5a that if $T_{s,o}$ or T_∞ are larger than certain values, the criterion $\Delta \geq \Delta_I$ will be immediately satisfied that the QSGP model yields zero ignition delay times.

The performance of the QSGP model for the evaporation of a nonvolatile hexadecane droplet is illustrated in Fig. 3. Due to the low fuel volatility, longer heating time is needed to reach a sufficiently high droplet surface temperature so that the Y_f distribution could build up to a significant level. The transient Y_f and T_g distributions can therefore develop closer to the QSGP ones during the longer period, as shown in Fig. 3a.

Droplet ignition takes place in the near-field gas phase during the early heating stage and is essentially transient in the gas as well as the liquid phase. The total ignition delay consists of a physical delay, during which the droplet is heated and the fuel vapor diffuses outward, and a chemical delay, which is the time required for the reactions to reach a runaway condition. The physical delay and chemical delay overlap essentially. When the QSGP assumption is employed, gas-phase-steady distributions of Y_f and T_g [Eqs. (4) and (5)] are assumed, with the process of transient fuel vapor diffusion ignored. Errors associated with the QSGP ignition model due to neglecting the transient diffusion process are expected to

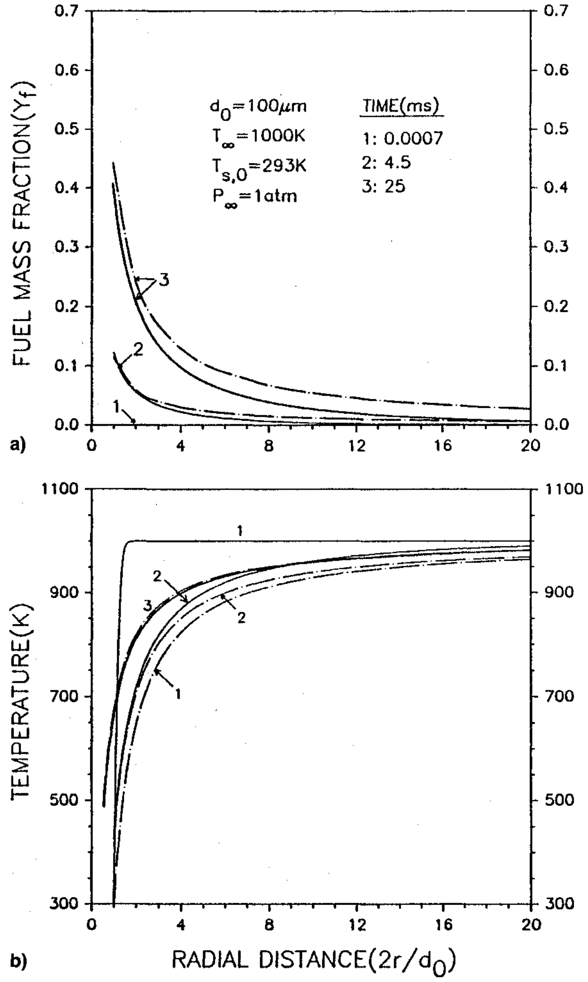

Fig. 3 Comparison of the distributions of fuel vapor concentration and gas temperature calculated by the transient and the QSGP analyses for an *n*-hexadecane droplet in an inert ambient: a) fuel mass fraction and b) gas temperature.

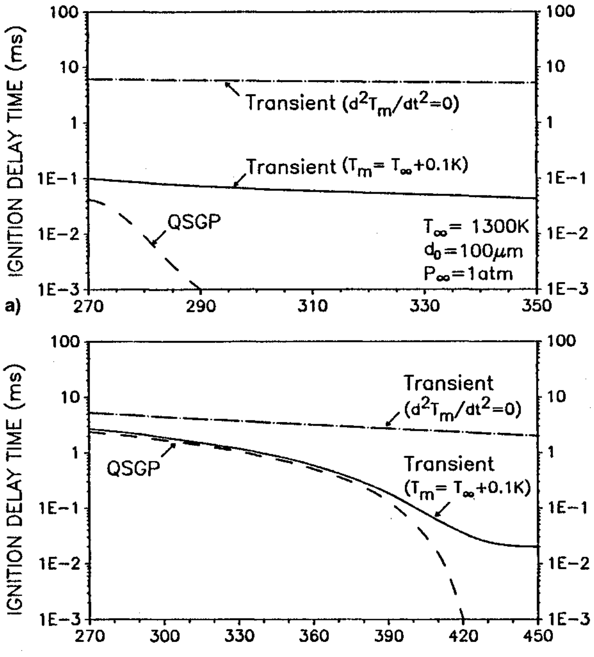

Fig. 4 Comparison of ignition delay times vs initial droplet temperature based on the transient and the QSGP analyses for: a) *n*-heptane and b) *n*-hexadecane droplets.

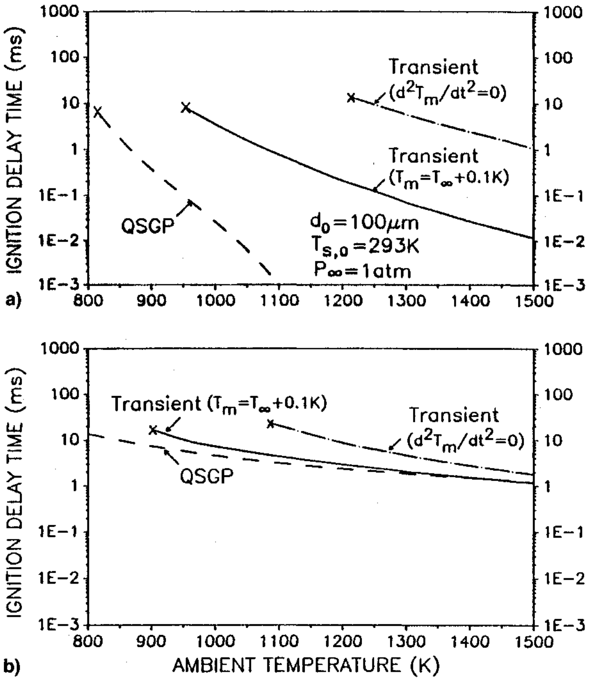

Fig. 5 Comparison of ignition delay times vs ambient temperature based on the transient and the QSGP analyses for a) *n*-heptane and b) *n*-hexadecane droplets.

be smaller for nonvolatile hexadecane than for volatile heptane. Since the preignition droplet heating times for nonvolatile fuel droplets are much longer the transient distributions of fuel vapor concentration and gas temperature could develop closer to the QSGP distributions. The suitability of QSGP assumption is specifically examined in the following with respect to fuel volatility, initial droplet temperature, ambient gas temperature, and droplet diameter.

Predictions of Ignition Delay Times

Figure 4 shows the QSGP and the transient ignition delay times vs initial droplet temperature $T_{s,o}$ for heptane and hexadecane droplets at T_∞ = 1300 K and d_0 = 100 μm. Since ignition defined in the QSGP ignition theory corresponds to the initiation of a temperature maximum in the gas phase, the appearance of $T_m = T_\infty + 0.1$ K is equivalently used in the transient calculations, as previously explained. Extremely large departure is obtained for heptane droplets (Fig. 4a). When $T_{s,o}$ is as low as 270 K, the QSGP ignition delay time is about half of the transient one with $T_m = T_\infty + 0.1$ K as the ignition criterion. As $T_{s,o}$ increases, the QSGP ignition model predicts immediate ignition when $T_{s,o}$ is higher than a certain value (presently about 290 K). Similar QSGP results have also been reported in Law.[3] Immediate ignition is physically unreasonable since the fuel vapor diffusion time is always required in spite of a large fuel vapor concentration at the droplet surface resulting from a high initial droplet temperature. It is not difficult to understand since the QSGP assumption ignores the vapor diffusion time and artificially imposes gas-phase-steady fuel vapor concentrations. For volatile heptane (boiling point = 371 K), consequently, at relatively low temperatures the corresponding far-field fuel concentration is already high enough that Δ_I is immediately satisfied. In contrast, the ignition delay times predicted by the transient ignition model decrease, but remain at finite values. Also shown are the ignition delay times determined by the transient analysis with $d^2T_m/dt^2 = 0$ as the ignition criterion. The ignition delay times thus calculated are longer than those with $T_m = T_\infty + 0.1$ K by a factor of about 100 for heptane droplets. For nonvolatile hexadecane droplets (Fig. 4b), the QSGP model yields immediate ignition at higher droplet temperatures ($T_{s,o} > 420$ K) because of the higher boiling point (560 K). For a fairly wide $T_{s,o}$ range, the ignition delay times predicted by the QSGP model agree well with those by the transient model with $T_m = T_\infty + 0.1$ K as the ignition criterion. If compared with the transient results with the criterion of $d^2T_m/dt^2 = 0$, the QSGP results appear underpredicted by a factor of at least four for the conditions examined.

The ignition delay times predicted, respectively, by the QSGP and the transient ignition model are plotted vs ambient temperature in Fig. 5 for both heptane and hexadecane. Extremely large departure exists between the QSGP and the transient results for heptane throughout the temperature range examined. When $T_\infty > 1100$ K, immediate ignition is predicted by the QSGP model. Although less departure is found at low-temperature, kinetically controlled conditions, the improvement is limited. Also compared are the transient ignition results associated with different ignition criteria. Again, the ignition delay times determined by $d^2T_m/dt^2 = 0$ are longer than those by $T_m = T_\infty + 0.1$ K by a factor of about 100 for the range of $T_\infty = 1200$–1500 K. For $T_\infty = 800$–1200 K, while ignition is predicted with the criterion of $T_m = T_\infty + 0.1$ K, complete vaporization before ignition is predicted with $d^2T_m/dt^2 = 0$. For hexadecane, the ignition delay results of the QSGP model are rather close to those of the transient model as long as ignition is defined as the initiation of a gas temperature maximum. However, if compared with the transient results based on the more rigorous ignition criterion $d^2T_m/dt^2 = 0$, the QSGP model yields acceptable results only for high-temperature conditions. The QSGP ignition delay times are still significantly underpredicted at low temperatures. Similar to the results for heptane droplets, there exists a temperature range ($T_\infty = 800$–1100 K) for which ignition is indicated by the QSGP model, but actually the droplets may have completely vaporized before ignition can be attained.

Figure 6 compares the QSGP and transient ignition delay times vs initial droplet diameter at $T_\infty = 1300$ K for both heptane and hexadecane. As in the previous cases, the QSGP results are severely underpredicted for heptane droplets and are rather close to the transient results corresponding to $T_m = T_\infty + 0.1$ K for hexadecane droplets. Compared with the transient results based on $d^2T_m/dt^2 = 0$, the QSGP model predicts significantly earlier ignition, except for large hexadecane droplets. Also, the QSGP model wrongly indicates the ignitability of small droplets that actually may have completely vaporized before ignition can be attained.

According to the previous investigations, the existing droplet ignition criteria,[2,3,5,8,9] which were derived based on the QSGP assumption without considering the transient FVA effects, are not suitable for the prediction of ignition delay times, as has been done in Refs. 3, 5, 11, and 19.

Predictions of Minimum Ignitable Temperatures

The performances of the QSGP and the transient ignition model concerning the minimum ignitable temperatures are discussed in Fig. 7. At an ambient temperature below the minimum ignitable temperature, the droplets will be completely vaporized before ignition can occur. Figure 7 indicates the following points:

1) The minimum ignitable temperatures, unlike ignition delay times, are essentially insensitive to fuel volatility. In fact, hexadecane droplets appear to have lower minimum ignitable temperatures than heptane droplets. It should be pointed out that the minimum ignitable temperatures determined relate to the kinetic parameters chosen, as indicated by Mawid and Aggarwal.[5]

2) The QSGP model yields lower minimum ignitable temperatures even when the initiation of a gas temperature maximum is used as the ignition criterion in both models.

3) The transient model with the criterion $d^2T_m/dt^2 = 0$ results in significantly higher minimum ignitable temperatures than with $T_m = T_\infty + 0.1$ K (by about 200–300 K for the conditions examined). This implies that there exists a temperature range within which chemical reactions may initiate gas temperature maximums, but are yet too weak to lead to thermal runaway before the droplets are completely vaporized. An example has been shown by Chao et al.[12]

4) Minimum ignitable temperatures decrease with increasing initial droplet diameter. For small droplets (e.g., $d_0 < 100$ μm), the droplet life times are so short that reactions have not been intensively activated to render ignition, even when

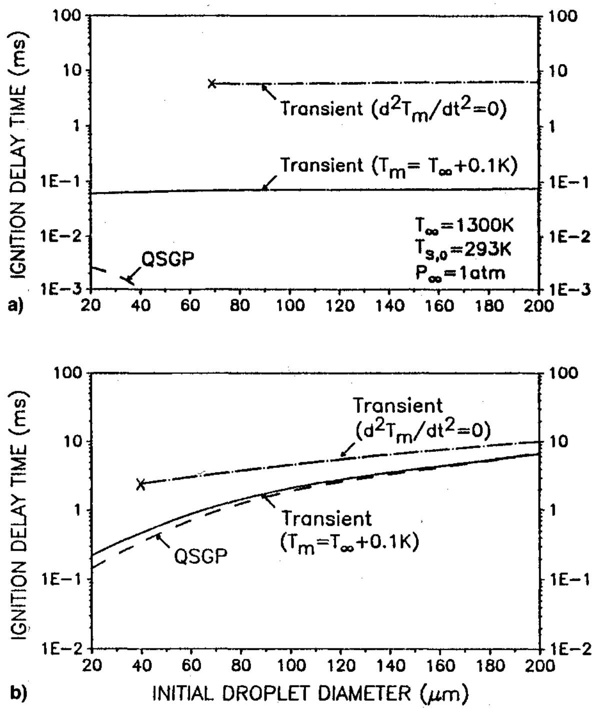

Fig. 6 Comparison of ignition delay times vs initial droplet diameter based on the transient and the QSGP analyses for a) *n*-heptane and b) *n*-hexadecane droplets.

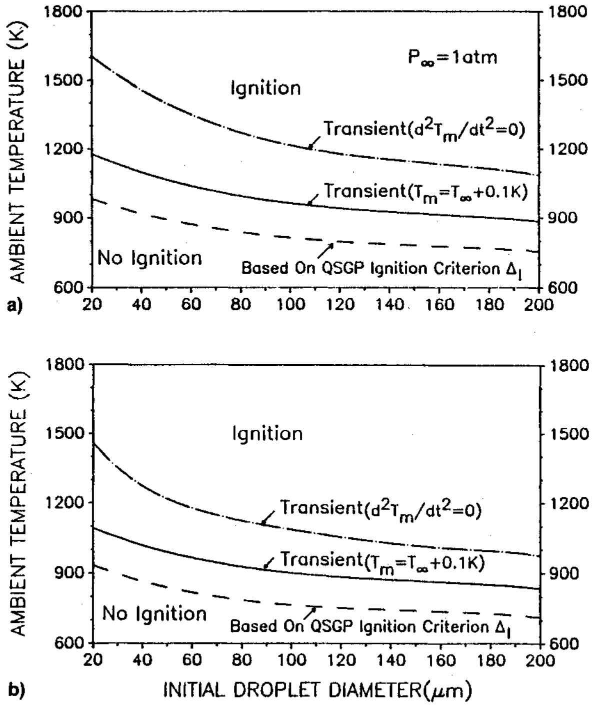

Fig. 7 Comparison of minimum ignition temperatures vs initial droplet diameter resulting from different ignition criteria for a) *n*-heptane and b) *n*-hexadecane droplets.

the ambient temperatures are relatively high. Minimum ignitable temperatures, therefore, depend on d_0 significantly for small droplets. For larger droplets the dependence on d_0 becomes weaker. This is because the ambient temperatures are too low to activate sufficiently strong reactions for ignition, even after rather long delay times. According to the previous investigations, the QSGP ignition criteria can be applied for determining the minimum ignitable temperatures, with the understanding that significant underestimations may exist.

Comparison with Experimental Data

Theoretical results are also compared with experimental data[16,20] in Figs. 8 and 9 for heptane and hexadecane droplets, respectively. These data were obtained under natural convection conditions, but, according to Faeth and Olson,[16] would differ from zero-gravity results only slightly. While the present kinetic parameters were determined by fitting Faeth and Olson's data at $T_\infty = 950$ K, the transient-model calculation of ignition delay times agrees quite well with the experimental data at $T_\infty = 1023$ K. The calculated minimum ignitable diameter at 950 K is about 550 μm, but the experimental value was not reported. As far as the performance of the QSGP model for heptane droplet ignition is concerned, we have been unable to fit the data with correct trend using the QSGP model. The calculated ignition delay times always decrease with increasing droplet diameters, which is contradictory to general observations. The best fit shown in Fig. 8 corresponds to kinetic parameters of $E_a = 38$ kcal/mole and $A = 5 \times 10^7$. This value of pre-exponential factor A is about 2000 times smaller than that for transient calculations.

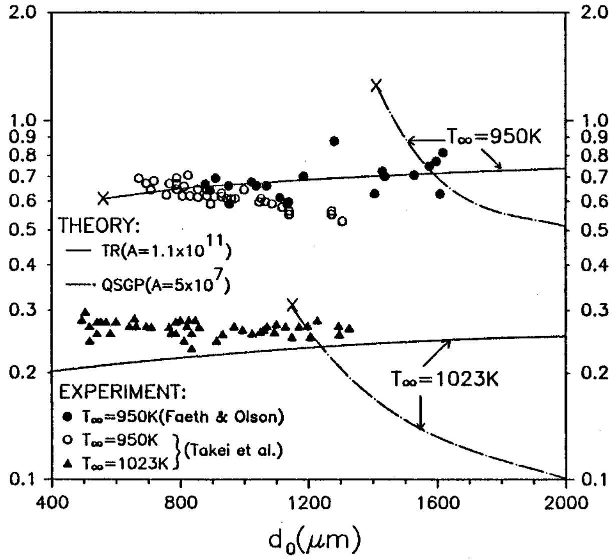

Fig. 8 Comparison of experimental ignition data with theoretical results by the transient and the QSGP analyses for n-heptane droplets.

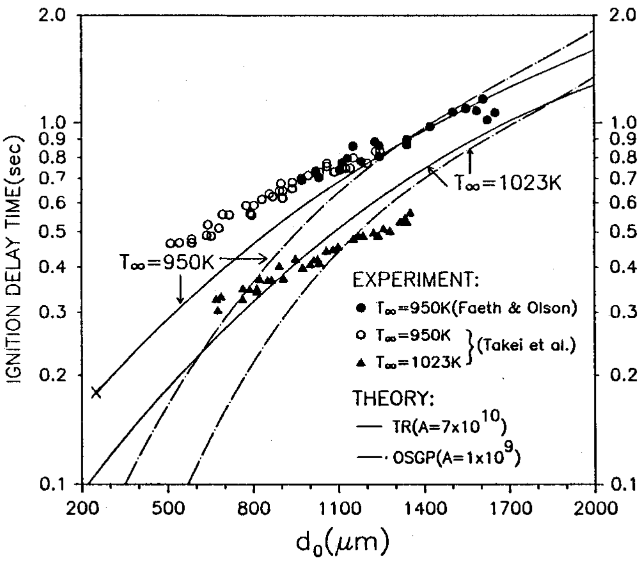

Fig. 9 Comparison of experimental ignition data with theoretical results by the transient and the QSGP analyses for n-hexadecane droplets.

Comparisons for hexadecane droplets are shown in Fig. 9. For the diameter range where experimental data are available, the agreement between the transient model and experimental results appears satisfactory with $A = 7 \times 10^{10}$. While no data of the minimum ignitable diameter are available, the theoretical results are about 200 μm for the conditions examined. The QSGP model prediction now exhibits correct trend with respect to diameter change, similar to the results of Mawid and Aggarwal.[5] However, the value of A for satisfactory fitting is only 1×10^9, which is 70 times smaller than that used in transient calculations. (Mawid and Aggarwal[5] obtained another set of kinetic parameters for hexadecane: $A = 1.19 \times 10^9$, $E_a = 45$ kcal/mole with $a_o = 1.5$ and $a_f = 0.25$.)

The reasons for the smaller values of A adopted in the QSGP calculations can be explained as follows. First, the Y_f distributions are unrealistically high due to ignoring the gas-phase transient diffusion process. Second, the QSGP ignition criterion corresponds to the appearance of a gas temperature maximum, which occurs somewhat earlier than the appearance of the first inflection in the T_m history, a physically more rigorous criterion. Therefore, when a QSGP ignition model is applied for ignition delay simulation, the values of the kinetic parameters must be reduced to counterbalance the overestimation of Y_f distribution and the early indication of ignition. For the same reasons, if the kinetic parameters used match the usually adopted values without being lowered, early ignition will be predicted. This can be found in Mawid and Aggarwal's[11] work, in which QSGP ignition criteria were applied to droplets in sprays. For a bicomponent fuel droplet the presence of only 10% volatile n-hexane results in drastic decreases of ignition delay times ($t_{ig} \cong 0.1$ ms for droplet diameters > 50 μm).

Conclusions

The following conclusions are reached in this study:

1) The QSGP ignition model, without considering the transient FVA effects, considerably underpredicts ignition delay times, particularly for more volatile fuels. The reasons are as follows: The reaction rates are considerably overestimated in the QSGP ignition analysis because the gas-phase transient FVA process is ignored and the mass conservation law is violated; and the ignition criterion employed in the QSGP analysis is the initiation of a temperature maximum in the gas phase, which is much less strict than the usual one, the appearance of the first inflection point in the maximum temperature history (i.e., $d^2T_m/dt^2 = 0$).

2) As far as minimum ignitable temperatures are concerned, for both heptane and hexadecane droplets the QSGP ignition model yields somewhat lower limits than those of the transient model with ignition also being defined as the initiation of a gas temperature maximum. However, if $d^2T_m/dt^2 = 0$ is used in the transient ignition analysis, the corresponding QSGP ignition limits appear to be significantly underestimated.

In summary, the existing QSGP ignition criteria, which were derived without considering the fuel vapor accumulation effects, are inappropriate for the determination of ignition delay times. Such criteria are valuable for the determination of the minimum ignitable temperatures, with the understanding that significant underestimations may exist.

Appendix A: Transient Droplet Ignition Model

The governing equations and initial and boundary conditions are as follows:

For liquid-phase equation $[r < R(t)]$

$$\frac{\partial \theta}{\partial t} = \alpha_l \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \theta}{\partial r} \right)$$

For gas-phase equations $[r > R(t)]$

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho u) = 0$$

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p u \frac{\partial T}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(k r^2 \frac{\partial T}{\partial r} \right) + \nu_f M_f Q \dot{\omega}$$

$$\rho \frac{\partial Y_i}{\partial t} + \rho u \frac{\partial Y_i}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(\rho D r^2 \frac{\partial Y_i}{\partial r} \right) - \nu_i M_i \dot{\omega}$$

$$(i = o \quad \text{or} \quad f)$$

where the Arrhenius kinetics is written as

$$\dot{\omega} = A \rho^{(a_f + a_o)} (Y_f / M_f)^{a_f} (Y_o / M_o)^{a_o} \exp(-E_a / R_u T)$$

The initial and boundary conditions are

$$\theta = \theta_0 \quad \text{at} \quad t = 0, \quad r < R(t)$$

$$T = T_\infty, \quad Y_f = 0, \quad Y_o = Y_{o\infty}, \quad u = 0$$

$$\text{at} \quad t = 0, \quad r > R(t)$$

At $r = 0$

$$\frac{\partial \theta}{\partial r} = 0$$

At $r = R(t)$

$$\begin{gathered} \theta = T \\ \rho_l L \frac{\mathrm{d}R}{\mathrm{d}t} = k_l \frac{\partial \theta}{\partial r} - k \frac{\partial T}{\partial r} \\ -\rho D \frac{\partial Y_f}{\partial r} = \rho u_s (1 - Y_{fs}) \\ \rho D \frac{\partial Y_o}{\partial r} = \rho u_s Y_{os} \\ u_s = \frac{\mathrm{d}R}{\mathrm{d}t} \left(1 - \frac{\rho_l}{\rho} \right) \\ Y_{fs} = Y_{fs}(T_s) \end{gathered} \tag{A1}$$

At $r \to \infty$

$$T = T_\infty, \qquad Y_f = 0, \qquad Y_o = Y_{o\infty}, \qquad u = 0$$

Instead of the Clausius–Clapeyron equation, we use the Cox equation[21] for Eq. (A1):

$$\ln(P/P_c) = [1 - (1/T_r)] \exp(C_1 + C_2 T_r + C_3 T_r^2)$$

where $T_r = T/T_c$, and $C_1 = 2.456$, $C_2 = -1.226$, and $C_3 = 0.782$ for *n*-heptane; and $C_1 = 2.897$, $C_2 = -1.569$, and $C_3 = 0.848$ for *n*-hexadecane.

The coordinate transformation and nondimensionalization follow Niioka et al.[13]

Nondimensional parameters are

$$\alpha^+ = \frac{\alpha_l}{\alpha}, \qquad E_a^+ = \frac{C_p \sigma_f E_a}{R_u Q}, \qquad k^+ = \frac{k_l}{k}, \qquad L^+ = \frac{M_f L}{R_u T_b}$$

$$r^+ = \frac{r}{R_0}, \qquad R^+ = \frac{R}{R_0}, \qquad S_t = \frac{Q \rho}{\sigma_f \rho_l L}, \qquad t^+ = \frac{\alpha t}{R_0^2}$$

$$T^+ = \frac{C_p \sigma_f T}{Q}, \qquad u^+ = \frac{R_0 u}{\alpha}, \qquad Y^+ = \sigma_i Y_i$$

$$\sigma_i = \frac{(\nu_o M_o + \nu_f M_f)}{\nu_i M_i}, \qquad \theta^+ = \frac{C_p \sigma_f \theta}{Q}$$

$$\rho^+ = \frac{\rho_l}{\rho}, \qquad D_a = \frac{A \rho^{(a_f + a_o - 1)} \nu_f^{a_f} \nu_o^{a_o} R_0^2}{\alpha (\nu_f M_f + \nu_o M_o)^{a_f + a_o - 1}}$$

Together with the following coordination transformation:

$$\xi = [r/R(t)], \quad \text{for} \quad r < R(t)$$

$$\eta = \ln[r/R(t)] = \ln \xi, \quad \text{for} \quad r > R(t)$$

we have the governing equations:

For liquid phase $(\xi < 1)$

$$\frac{\partial \theta^+}{\partial t^+} = \alpha^+ \frac{1}{R^{+2}} \frac{\partial^2 \theta^+}{\partial \xi^2} + \left(\frac{\xi \dot{R}^+}{R^+} + \frac{\alpha^+}{R^{+2}} \frac{2}{\xi} \right) \frac{\partial \theta^+}{\partial \xi} \tag{A2}$$

For gas phase $(\eta > 0)$

$$\mathscr{L}(T^+, 1, -1) = 0 \tag{A3}$$

$$\mathscr{L}(Y_i^+, L_e, 1) = 0 \tag{A4}$$

where the operator $\mathscr{L}$ represents

$$\begin{aligned} \mathscr{L}(\Phi, m, n) = {} & \frac{\partial \Phi}{\partial t^+} - \frac{1}{m(R^+ e^\eta)^2} \frac{\partial^2 \Phi}{\partial \eta^2} \\ & - \left[\frac{1}{m(R^+ e^\eta)^2} + \frac{\dot{R}^+}{R^+} - \frac{u^+}{R^+ e^\eta} \right] \frac{\partial \Phi}{\partial \eta} \\ & + n D_a Y_o^{+a_o} Y_f^{+a_f} \exp\left(-\frac{E_a^+}{T^+} \right) \end{aligned} \tag{A5}$$

In Eq. (A5)

$$u^+ = u_s^+ \exp(-2\eta)$$

The initial and boundary conditions become

$$\begin{gathered} \theta^+ = \theta_0^+, \qquad t^+ = 0, \quad \xi < 1 \\ T^+ = T_\infty^+, \quad Y_f^+ = 0, \quad Y_o^+ = Y_{o\infty}^+, \quad u^+ = 0 \\ t^+ = 0, \quad \eta > 0 \end{gathered} \tag{A6}$$

At $\xi = 0$

$$\frac{\partial \theta^+}{\partial \xi} = 0 \tag{A7}$$

At $\xi = 1$

$$\theta_s^+ = T_s^+ \tag{A8}$$

$$\frac{\mathrm{d}R^+}{\mathrm{d}t^+} = \frac{S_t}{R^+} \left(k^+ \frac{\partial \theta^+}{\partial \xi} - \frac{\partial T^+}{\partial \eta} \right) \tag{A9}$$

$$-\frac{\partial Y_f^+}{\partial \eta} = L_e u_s^+ R^+ (\sigma_f - Y_{fs}^+) \tag{A10}$$

$$\frac{\partial Y_o^+}{\partial \eta} = L_e u_s^+ R^+ Y_{os}^+ \tag{A11}$$

$$u_s^+ = \frac{\mathrm{d}R^+}{\mathrm{d}t^+}(1 - \rho^+) \tag{A12}$$

$$Y_{fs}^+ = Y_{fs}^+(T_s^+) \tag{A13}$$

At $\eta \rightarrow \infty$

$$T^+ = T_\infty^+, \quad Y_f^+ = 0, \quad Y_0^+ = Y_{o\infty}^+, \quad u^+ = 0 \tag{A14}$$

Equations (A2–A14) are solved numerically by using the finite difference method.

Appendix B: Quasisteady Droplet Ignition Criterion

According to the QSGP ignition theory of Law[2,3] a droplet of given properties vaporizing in an environment achieves ignition if the system Damköhler number Δ exceeds the ignition Damköhler number Δ_I, i.e.,

$$\Delta \geq \Delta_I(\beta)$$

For nonunity-exponent kinetics, according to Mawid and Aggarwal[5]

$$\Delta = \left[\frac{A(M_f)^{1-a_f}}{\rho_\infty D_\infty (M_o)^{a_o}} \left(\frac{PC_p}{R'Q}\right)^{a_o+a_f}\right] \times \left[\frac{Y_{o\infty}^{a_o} \exp(-T_a/T_\infty)(\hat{m}R_s)^2}{\left(\dfrac{C_p T_\infty}{Q}\right)^{a_o+a_f} \left(\dfrac{C_p T_\infty^2}{T_a Q}\right)^{3-a_f}}\right] \tag{B1}$$

with $a_f = 0.25$, $a_o = 1.5$, and according to Makino[8]

$$\Delta_I = \frac{1}{2\Gamma(1.25)}\left[\frac{4}{e(1-\beta)}\right]^4 - 0.68\left[\frac{4}{e(1-\beta)}\right] \tag{B2}$$

where

$$\Gamma(1.25) = 0.90640$$

The nondimensional parameters appearing in Eqs. (B1) and (B2) are defined as

$$\begin{aligned} \hat{m} &= \ln(\beta/\hat{H}), \qquad \beta = \hat{T}_\infty - \hat{T}_s + \hat{H} \\ \hat{T} &= C_p T/Q, \qquad \hat{H} = H/Q \end{aligned} \tag{B3}$$

The quantities of $\hat{m}$, $\hat{T}_s$, and R_s required in Eqs. (B1) and (B2) are obtained from liquid-phase solutions. In both the transient and the QSGP model, conduction-limit analysis is adopted for the liquid phase.

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