

# Droplet Vaporization in Subcritical and Supercritical Environments; High vs Low Pressure Modeling

Gurnam Singh<sup>1</sup> and Neel Kanth Grover<sup>2</sup>

<sup>1</sup>Department of Mechanical Engineering, S.B.S.S.T.C., Ferozepur, Punjab, India.  
E-mail: [gsm\\_377@rediffmail.com](mailto:gsm_377@rediffmail.com)

<sup>2</sup>Department of Mechanical Engineering, IKPTU, Kapurthala, Punjab, India.  
E-mail: [neelkanthgrover@rediffmail.com](mailto:neelkanthgrover@rediffmail.com)

## Abstract

Droplet vaporization under high-pressure stagnant conditions has been studied numerically. Computations have been performed using both a high pressure (HP) and a low pressure (LP) model. Results are presented for an n-heptane droplet evaporating into a nitrogen environment, for initial temperature of 300 K, and various ambient pressures and temperatures. It is predicted that at higher pressures the droplet surface temperature keeps rising until the end of the droplet lifetime. Compared to the HP model, the LP model over predicts the droplet lifetime, the deviation increasing with pressure. The predictions show that the droplet lifetime decreases monotonically with increase in ambient temperature at all the ambient pressures. At subcritical ambient temperatures, the droplet lifetime increases as the ambient pressure is increased and at supercritical ambient temperatures, the droplet lifetime decreases with increase in pressure.

**Keywords:** Droplet, evaporation, ignition, pressure

## INTRODUCTION

In diesel and spark-ignited direct injection combustion engines and gas turbine combustors, fuel is introduced in the combustion chamber by spray injection, which, for a given injector and operating conditions, produces droplets. These droplets break-up into smaller droplets and the liquid fuel is vaporized, producing local regions of stoichiometric mixtures of vaporized fuel and air. The rate at which these hydrocarbon fuel droplets vaporizes strongly affects the formation of these stoichiometric regions. Therefore an understanding of this process is of critical importance in modeling the spray process and thus the combustion process. As supercritical conditions of the vaporization are prevalent for many fuel components, thus the subcritical models for vaporization are not suitable to be applied. An understanding of the vaporization process engines and rockets can result in changes in the design of injectors and combustion chambers to improve efficiency and trim down emissions. Thus, there appears a need for an accurate model to predict supercritical vaporization of hydrocarbon droplets.

The classical studies on the evaporation of a droplet [1,2] used the assumptions of gas phase quasi-steadiness, ideal gas behavior, and insolubility of gas in the liquid phase amongst others. With these assumptions, the problem of an evaporating droplet had been solved and is called as the  $D^2$  law. Chin and

Lefebvre [3] studied the effect of ambient pressure on the evaporation of a single droplet using classical model. They showed that the rate of evaporation increased with ambient pressure when the ambient temperature was high (supercritical), but decreased with pressure at lower temperatures (subcritical).

An extensive review of studies at supercritical ambient conditions has been provided by Gilver and Abraham [4]. They suggested that the approximation of quasi-steadiness in the gas phase was not valid for paraffins if the reduced temperature and pressure exceeded approximately twice the fuel's critical values. They further suggested that other major modeling assumptions were needed near the critical region, for example, on the effect of a gas being real, the effect of liquid-phase gas solubility, and anomalies in thermophysical properties.

Zhu and Aggarwal [5] numerically calculated the rate of evaporation of a droplet in a supercritical environment. The model accounted for gas and liquid phase unsteadiness, pressure dependent thermophysical properties and solubility of gases in liquid phase. They showed that predictions using Peng-Robinson equation of state PR-EOS agrees well with the experimental data. All the studies for high pressure evaporation deals with single component droplet.

Nomura et al. [6] showed that an evaporating droplet does not reach a critical mixing state immediately whenever ambient conditions exceed the critical point of the fuel. Curtis and Farrell [7,8] showed that anomalies in the transport properties near the critical mixing state were insignificant under the conditions of Diesel ignition. Ruszalo and Hallett [9] investigated numerically the ignition of a droplet at high pressures and showed that the ignition delay time decreases at higher pressures, but the effect on ignition of a gas being soluble in the liquid-phase was small.

Delpaque and Sirignano [10] also considered a transient, spherically-symmetric model to investigate transient gasification of a liquid oxygen droplet in gaseous hydrogen at high pressures. It was noted that at supercritical pressures, the droplet surface temperature reaches the critical mixing value. Jia and Gogos [11,12] employed the PR-EOS to quantify the effect of liquid phase gas solubility on the vaporization of a n-hexane droplet for a range of ambient pressures and temperatures. It was shown that the liquid-phase gas solubility becomes increasingly important as the ambient pressure approaches the critical value. In addition, the variation of droplet lifetime with pressure was shown to exhibit a

maximum at low ambient temperatures, but to decrease monotonically with pressure at high ambient temperatures. Stengel et al. [13] employed the SRK-EOS to examine the vaporization behavior of freely falling n-heptane droplets in a nitrogen environment. Results from a quasi-steady droplet model were compared with measurements for ambient pressure up to 40 atm. Aggarwal et al. [14] also reported a quasi-steady high-pressure model that used the PR-EOS and included the transient liquid-phase processes, as well as the effect of pressure on thermo-physical properties. The predicted vaporization histories were shown to compare well with the measurements of Stengel et al. [13].

The goal of the present study is to examine various aspects that add tremendously to the complexity and uncertainty of a comprehensive high pressure droplet vaporization model. There is a need for such an elaborate model yet it must be of moderate complexity so that it can be used in a large spray code. First, the importance of dissolved ambient gas into the liquid droplet needs to be examined. Allowing for gas solubility in the droplet interior makes the calculation for the vapor-liquid equilibrium composition and for the energy required for phase change at the droplet surface extremely complex.

Further more, the species equation in the liquid phase needs to be solved. In addition to the complexity, the limited information on binary diffusion coefficients in the liquid phase, and the use of the equation of state in the liquid phase for composition calculations at the droplet surface add uncertainties to the model. The aim of this study is to develop a model for evaporation to determine the effect of pressure and investigate the effect of ambient pressure on the evaporation of a single droplet and also a spray.

This study presents a thorough validation of the comprehensive numerical model with the experimental results of Nomura et al. [6]. The results for a vaporizing stationary droplet under zero-gravity for a wide range of ambient pressures and temperatures have been presented in detail. The goal of the study is to present a detailed high pressure model (HP) and to compare the results with low pressure (LP) model for a wide range of ambient pressures and temperatures.

## MODEL

The following assumptions are made to model the problem: Spherical symmetry and constant pressure, momentum equation is not solved in the gas phase as the pressure is assumed to be constant, Soret and Dufour effects are neglected, the radial velocity, which is non zero, has been evaluated from the continuity equation.

### A. Governing equations

The liquid phase energy and species equation are given as

$$\frac{\partial \theta}{\partial t} + \frac{1}{\rho_l c_{p,l} r^2} \frac{\partial}{\partial r} \left( k_l r^2 \frac{\partial \theta}{\partial r} \right) = 0 \quad (1)$$

$$\frac{\partial Y_{f,i,l}}{\partial t} - \frac{D_l}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial Y_{f,i,l}}{\partial r} \right) = 0 \quad (2)$$

With uniform pressure in the gas phase, the momentum equation is trivially satisfied and the gas velocity can be obtained from mass conservation without solving the momentum conservation [14]. The gas phase conservation equations of mass, species and energy are:

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho v) = 0 \quad (3)$$

$$\rho \frac{\partial Y_{f,i}}{\partial t} + \rho v \frac{\partial Y_{f,i}}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( \rho D_{f,i} r^2 \frac{\partial Y_{f,i}}{\partial r} \right) \quad (4)$$

$$\rho c_{p,g} \frac{\partial T}{\partial t} + \rho c_{p,g} v \frac{\partial T}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 k_g \frac{\partial T}{\partial r} \right) \quad (5)$$

### B. Initial and boundary conditions

Initially, the droplet is at a uniform temperature equal to the standard ambient temperature, i.e., 298.15 K and with homogeneous initial composition. The boundary conditions at the droplet center ( $r = 0$ ) are:  $\frac{\partial Y_{i,l}}{\partial r} = 0$ ,  $\frac{\partial \theta}{\partial r} = 0$  and at outer boundary ( $r \rightarrow \infty$ ) are:  $T = T_\infty$ ,  $Y_i = Y_\infty$ . At the droplet surface the conditions of species, energy and thermodynamic equilibrium are represented as:

$$\left[ \dot{m}'' Y_{i,l} - \rho_l D_l \frac{\partial Y_{i,l}}{\partial r} \right]_{r=R_s^-} = \left[ \dot{m}'' Y_i - \rho_g D_i \frac{\partial Y_i}{\partial r} \right]_{r=R_s^+} \quad (7)$$

$$k_g \left( \frac{\partial T}{\partial r} \right)_{r=R_s^+} = k_l \left( \frac{\partial \theta}{\partial r} \right)_{r=R_s^-} + \sum_{i=1}^N \left[ \dot{m}'' Y_i - \rho_g D_i \frac{\partial Y_i}{\partial r} \right]_{r=R_s^+} \Delta H_{v,i} \quad (8)$$

Thermodynamic vapor-liquid phase equilibrium exists at the droplet surface. At low ambient pressures, the solubility of the ambient gas in the liquid phase is neglected; consequently the phase equilibrium is represented by using Clausius-Claperyon relation. But, for higher pressures, following equilibrium relations are required:

$$T = \theta \quad (9)$$

$$p^v = p^l \quad (10)$$

$$f_i^v = f_i^l \quad (11)$$

### C. Numerical scheme

Due to spherical symmetry, the present simulation is one-dimensional with a regular boundary. The Crank-Nicolson method has been used for the discretization of second derivative; which is second order accurate in both time and space. As the problem is non-linear, Newton's method has been used for linearizing the discretized equations. Discretization of the model equations results in a tridiagonal system of algebraic equations which can be solved by Thomas Algorithm. Using this algorithm, the number of basic arithmetic operations for solving a tridiagonal set is of the

order of  $N$ , in contrast to  $O(N^3)$  operations required for solving with Gauss Elimination method. Therefore, not only is the computation time much shorter, but the roundoff errors are also significantly reduced [32]. At the center of the droplet, i.e., at  $x = 0$ ,  $\frac{\partial \theta^+}{\partial x} = 0$  which results in a singularity. Special care has been taken to address this issue by do away with this problem by dealing with derivative boundary conditions at drop center. Fictitious nodes were considered in order to apply second order accurate central differencing [32]. After coding, several simulations were performed to ascertain the sensitivity of grid size and time step. Saitoh and Nagano [31] used a relatively large grid size of 0.16 in their calculations for a domain of size  $0 \leq \eta \leq 8.0$ . Here, trial runs were performed for a small grid size of  $\Delta\eta = 0.1, 0.05, 0.025, 0.020$  and  $0.0125$  for droplet lifetime estimation and droplet surface temperature. The solution became invariant for grid size of  $\Delta\eta = 0.025, 0.020$  and  $0.0125$ . Therefore, a grid size of  $\Delta\eta = 0.025$  was considered to be appropriate. The type of numerical method and the fine mesh employed necessitated the adoption of very small time step sizes. A higher value of time step of the order of  $10^{-4}$  resulted in numerical instabilities. Therefore, at the start of a simulation a non-dimensional time step of  $\Delta t = 1 \times 10^{-6}$  was used which was increased as the simulation progressed.

## RESULTS AND DISCUSSION

Results have been presented for n-heptane droplet evaporating into different nitrogen environments. Before the presentation of results, the predictions have been validated against the available experimental data for vapor liquid equilibrium at the droplet surface. Figure 1 presents the predicted phase equilibrium in terms of variation of nitrogen mole fraction with ambient pressure. The results are in close agreement with the experimental results of Knapp et.al. [ ]. Figure 2 shows the comparison of predictions of both high pressure model (HP) and low pressure (LP) model with the experimental data of Nomura et. al [ ]. Results have been presented in terms of temporal variation of non-dimensional surface area for three different ambient conditions. It is evident that the HP model can reproduce the experimental data over a wide range of pressure and temperature. The LP model under-predicts the droplet surface regression and thus over-predicts the droplet lifetime. This effect tends to be more pronounced at higher pressure. The results also predicts that as the pressure increases, the droplet heat up time is more prominent in droplet lifetime as the liquid boiling point increases with increase in ambient pressure. The results also predicts that as the pressure increases, the droplet heat up time is more prominent in droplet lifetime as the liquid boiling point increases with increase in ambient pressure.

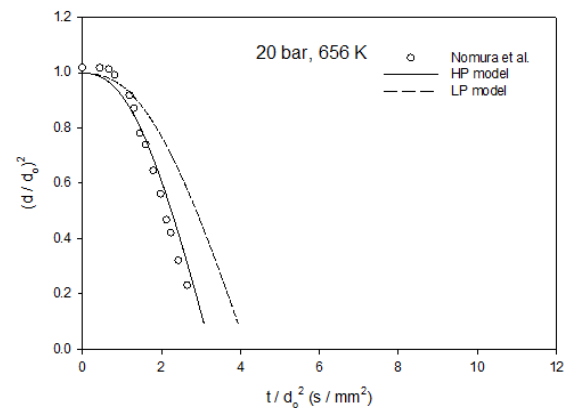
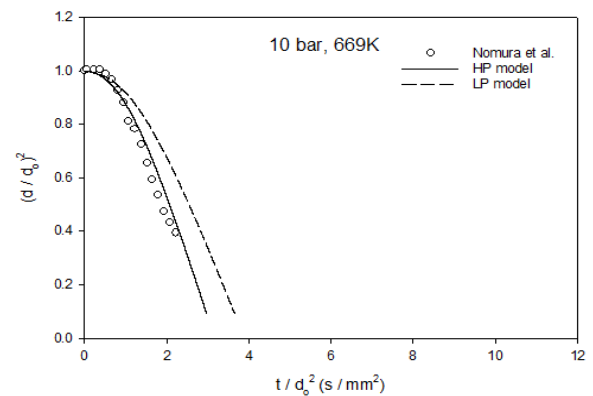
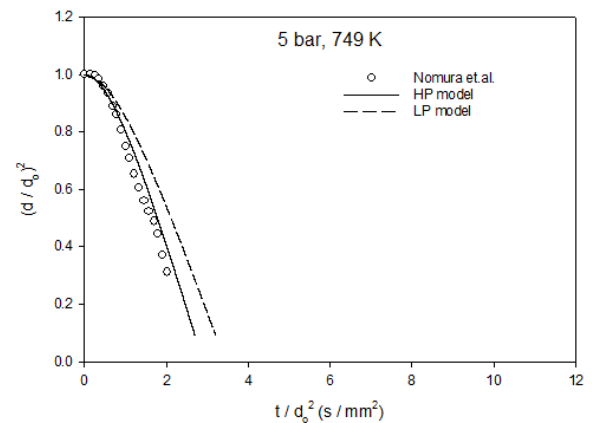
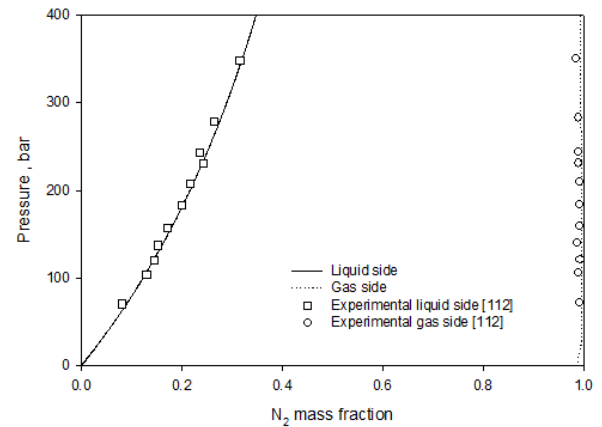
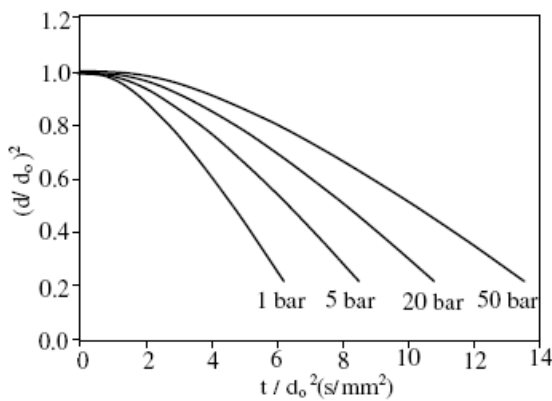
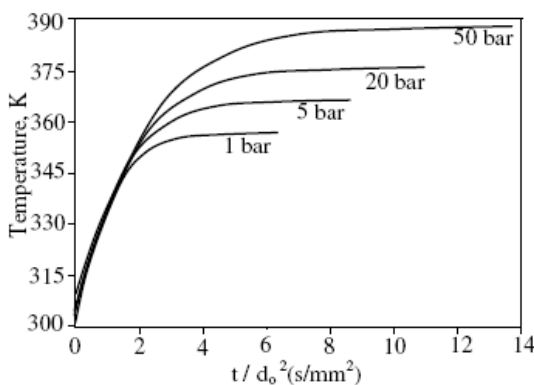


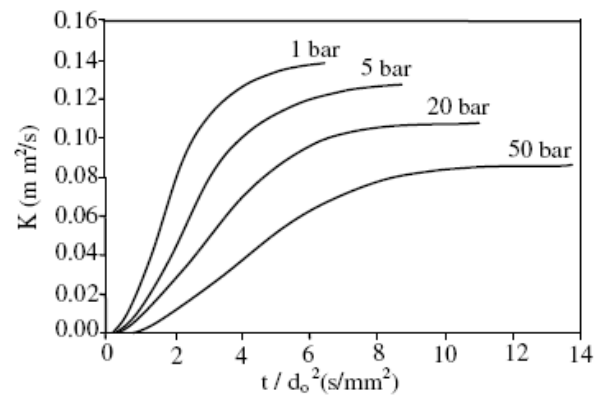
Figure 3 presents the time histories of the non-dimensional droplet diameter squared (Fig. 3a), evaporation constant (Fig. 3b) and the temperature (Fig. 3c) at the droplet surface for different ambient pressures and at a relatively low ambient temperature (450 K). Figure 3a shows that the time history of  $(d/d_o)^2$  follows  $d^2$ -Law for all the ambient pressures considered, except during the initial heat-up period. The droplet lifetime increases with increasing pressure at this low ambient temperature. The evaporation constant sharply increases during the heat-up period and reaches a constant maximum value (Fig. 3b). However, the maximum value decreases with increasing pressure. The temporal variation of surface temperature  $T$  is shown in Fig. 3c, where both the droplet surface and the droplet center temperatures reach a constant maximum value after the initial heat-up period. The maximum droplet temperature increases with increasing pressure. At this low ambient temperature, due to the increase in the droplet surface temperature with pressure, the rate of heat transfer to the droplet is reduced with increasing ambient pressure. As a result, the evaporation constant decreases with increasing pressure. It should be noted that the energy required for phase change decreases with increasing pressure. Due to this the evaporation constant is expected to increase. However, the effect of the reduction in the heat transfer rate discussed above dominates, leading to net decrease of the maximum evaporation constant. At a relatively high ambient temperature ( $T = 750 K$ ), entirely different trends of variations in the quantities discussed in Fig. 3, are seen.



(a)



(b)

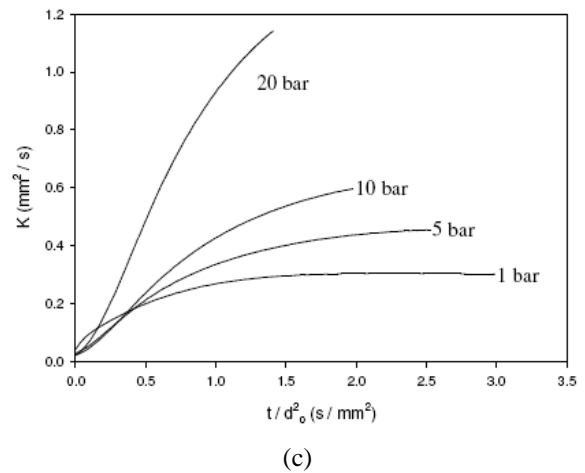
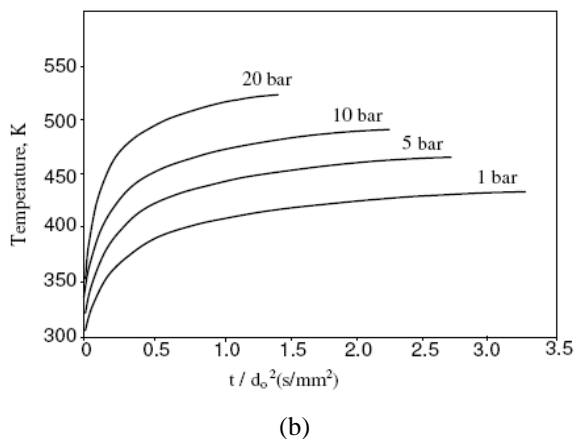
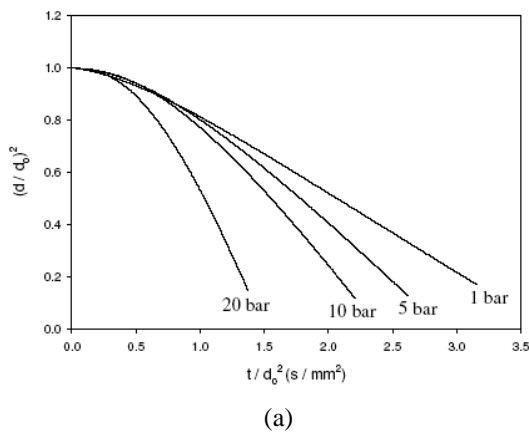


(c)

**Figure 3:** Time histories of (a)  $(d/d_o)^2$ , (b) Surface temperature, (c) Evaporation constant at different ambient pressures and  $T = 450 K$

Figure 4 shows the temporal variations of  $(d/d_o)^2$ , evaporation constant, and droplet surface temperature for this high ambient temperature case. It is clear from Fig. 4a that the slopes of the  $(d/d_o)^2$ , curves change continuously with time and the  $d^2$ -Law is no longer valid. Also, the droplet lifetime decreases with increasing ambient pressure, unlike the low ambient temperature case. Figure 4b shows that the evaporation constant  $K$  never reaches a constant value and its variation is highly transient through out the droplet lifetime, especially at high pressures. Even for the lowest pressure considered, only towards the end of the droplet lifetime, the value of  $K$  tends to reach a constant value (Fig. 4b). For this high ambient temperature case, the relative increase in the  $K$  value at higher pressures is due to the fact that at high pressure and high temperature, the energy required for phase change is lower, and this speeds up the vaporization process. The droplet temperature increases with (Fig. 4c). This causes a reduction in the heat transfer rate as discussed before. However, the effect of decrease in the energy requirement for the phase change for this high ambient temperature case overcomes the reduction in the heat transfer rate as discussed before. However, the effect of decrease in the energy requirement for the phase change for this high ambient temperature case overcomes the reduction in the heat transfer rate. As a result, for this case the constant  $K$  never reaches a constant value and its variation is highly transient through out the droplet lifetime, especially at high pressures. Even for the lowest pressure considered, only towards the end of the droplet lifetime, the value of  $K$  tends to reach a constant value (Fig. 4b). For this high ambient temperature case, the relative increase in the  $K$  value at higher pressures is due to the fact that at high pressure and high temperature, the energy required for phase change is lower, and this speeds up the vaporization process. The droplet temperature increases with pressure (Fig. 4c). This causes reduction in the heat transfer rate as discussed before. However, the effect of decrease in the energy requirement for the phase change for this high ambient temperature case overcomes the reduction in the heat transfer rate. As a result,

for this case the evaporation constant value increases with increasing pressure. As far as droplet temperature is concerned, the transient heat-up period extends almost up to the complete lifetime of the droplet (Fig. 4c), unlike the previous case (Fig. 3c). It is clear from Fig. 4c that for the highest pressure considered both the droplet surface and the center temperature increase with time continuously. Only for the lowest pressure considered and only near the end of the droplet lifetime, the temperature at the droplet center asymptotically approaches the surface temperature. As the pressure increases, transient effects are present for a longer time. It may be noted that at the highest pressure considered, not even the surface mass fraction of nitrogen reaches a constant value like what happens at the other lower pressures. As seen earlier, at low ambient temperatures and pressures, the evaporation constant reaches a maximum and constant value (Fig. 3b) soon after the heat-up period. However, at elevated ambient temperatures and pressures, transient effects are present till the end of the droplet lifetime (Fig. 3b). At super-critical ambient temperatures, the average evaporation constant value increases with the ambient pressure, which is in agreement with the experimental observations of Nomura et al. [6]. As discussed earlier with respect to Fig. 4, the reason for this trend is that the effect of the decrease in the energy requirement for the phase change overcomes the effect of the decrease in the rate of heat transfer due to increase in the droplet temperature.



**Figure 4:** Time histories of (a)  $(d/d_0)^2$ , (b) Surface temperature, (c) Evaporation constant at different ambient pressures and  $T = 750\text{ K}$

## CONCLUSIONS

A comprehensive numerical model has been developed to study droplet evaporation over a wide range of ambient temperatures and pressures. The model captures the transient high pressure vaporization process, by employing temperature and pressure dependent variable thermo-physical properties in the gas- and the liquid-phases, the real gas effects and the solubility of inert species into the liquid phase. The unsteady equations of mass, species and energy conservation in spherically symmetric coordinates are solved using the finite-difference method. The spherically symmetric numerical model has been thoroughly validated against the extensive microgravity experimental data of Nomura et al. [6]. The numerical model with negligible droplet velocity has been used to simulate the spherically symmetric droplet vaporization process. The main predictions are listed below: The LP model fails to validate the experimental observations and the deviation increases with the increase in pressure. The HP model validates the high pressure experimental results. The energy required for phase transfer decreases with increasing ambient pressure and temperature. At a low ambient temperature (sub-critical), thermodynamic equilibrium is attained after a short heat-up period and the droplet lifetime increases with increasing pressure. Also, for this sub-critical ambient temperature case, the effect of decrease in the rate of heat transfer due to the increase in the droplet temperature at high pressures is seen to dominate the effect of reduction in the phase change energy requirement. As a result, the evaporation constant decreases with increasing ambient pressure. On the other hand, when a super-critical ambient temperature is considered, the droplet lifetime decreases with increasing ambient pressure. Furthermore, the effect of the reduction in the energy requirement for the phase change is seen to dominate the effect of decrease in the rate of heat transfer. As a result, the evaporation constant increases with ambient pressure. The transient droplet heat-up period prevails until the end of the droplet lifetime at high ambient pressures and temperatures.

LIST OF SYMBOLS

$c$	Constant pressure specific heat of gas
$D_i$	Diffusion coefficient of species $i$
$d$	Diameter
$d_o$	Initial diameter of droplet
$d_i$	Instantaneous droplet diameter
$f$	Fugacity
$h_f^o$	Standard heat of formation of species $i$
$k$	Thermal conductivity
$m$	Mass
$\dot{m}$	Mass flow rate
$\dot{m}''$	Mass per unit area or heat flux
$P$	Pressure
$P_r$	Reduced pressure, $\frac{P}{P_c}$
$r$	Radial Distance
$R_u$	Universal gas constant
$R_o$	Initial droplet radius
$R(t)$	Instantaneous droplet radius
$t$	Time
$T$	Temperature in gas phase
$T_b$	Boiling temperature of liquid fuel
$T_r$	Reduced temperature, $\frac{T}{T_c}$
$v$	Radial velocity
$V$	Volume
$W_i$	Molecular weight of species $i$
$Y_i$	Mass fraction of species $i$ in gas phase

Subscripts

$c$	At critical conditions
$s$	At drop surface
$\infty$	At infinity
$f$	Fuel
$g$	Gas phase
$i, j$	Species
$in$	Initial
$l$	Liquid phase
$m$	mixture
$O$	oxidizer
$o$	At standard ambient conditions

$v$  Fuel vapor

Superscripts

$o$  At atmospheric pressure

Greek symbols

$\phi$  Fugacity coefficient

$\eta$  Transformed coordinate in gas phase

$\kappa$  Frequency factor

$\theta$  Temperature in liquid phase

$\rho$  Density

REFERENCES

- [1] G. M. Faeth, Current status of droplet and liquid combustion, *Progress in Energy and Combustion Science*, vol. 3, pp. 191 - 224, 1977.
- [2] C. K. Law, Recent advances in droplet vaporization and combustion, *Progress in Energy and Combustion Science*, vol. 8, pp. 171 - 201, 1982.
- [3] J. S. Chin, A. H. Lefebvre, *International Journal for Turbo Jet Engines*, vol. 2, pp. 315, 1985.
- [4] S. D. Givler, and J. Abraham, Supercritical droplet vaporization and combustion studies. *Progress in Energy and Combustion Science*, vol. 22, pp. 1-28, 1996.
- [5] G. S. Zhu, and S. K. Aggarwal, Transient supercritical droplet evaporation with emphasis on the effects of equation of state, *International Journal for Heat and Mass Transfer*, vol. 43, pp. 1157 - 1171, 2000.
- [6] H. Nomura, Y. Ujiie, H.J. Rath, J. Sato, and M. Kono, Experimental study of high-pressure droplet evaporation using microgravity conditions, *Twenty-Sixth Symposium (International) on Combustion*, The Combustion Institute, pp. 1267-1273, 1996.
- [7] E.W. Curtis, and P.V. Farrell, Droplet vaporization in a supercritical microgravity environment, *Acta Astronautica*, vol. 17, pp. 1189 -1193, 1988.
- [8] E.W. Curtis, and P.V. Farrell, A numerical study of high- pressure droplet vaporization, *Combustion and Flame*, vol. 90, pp. 85 - 102, 1992.
- [9] R. Ruszalo, and W.L.H. Hallett, A model for the autoignition of single liquid droplets at high pressure, *Combustion Science and Technology*, vol. 86, pp. 183 - 197, 1992.
- [10] J.P. Delplanque, and W.A. Sirignano, Numerical study of the transient vaporization of an oxygen droplet at sub and super-critical conditions, *International Journal for Heat and Mass Transfer*, vol. 36, pp. 303 - 314, 1993.

- [11] H. Jia, and G. Gogos, Investigation of liquid droplet evaporation in subcritical and supercritical gaseous environments, *Journal of Thermophysics and Heat Transfer*, vol. 6, pp. 738 – 745, 1992.
- [12] H. Jia, and G. Gogos, High pressure droplet vaporization; effects of liquid-phase gas solubility, *International Journal for Heat and Mass Transfer*, vol. 36, pp. 4419 – 4431, 1993.
- [13] S.K. Aggarwal, Z. Shu, H. Mongia, and H.S. Hura, Multicomponent and single-component fuel droplet evaporation under high pressure conditions, *AIAA Paper No. 98-3833*, 1998.
- [14] N. K. Grover, Numerical studies on multicomponent droplet evaporation and combustion at normal and high ambient pressures, *PhD Thesis, Indian Institute of Technology Delhi*, 2009.
- [15] H. Zhang, Evaporation of a Spherically Moving Fuel Droplet Over a Wide Range of Ambient Pressures Within a Nitrogen Environment, *Ph.D Thesis, University of Nebraska-Lincoln*, 2000.