Preliminary Experimental and Numerical Studies on Supercritical Ethylene Condensation

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ABSTRACT
Injection of supercritical fuel has become an increasingly important research area in the development of advanced air-breathing propulsion systems. The condensed phase can be generated through the homogeneous nucleation process within the supercritical jets at injection conditions close to the thermodynamic critical state. Injection of the condensed phase can potentially impact the combustion behavior of the engine. In this study, the structures of condensed supercritical ethylene jets injected from an axisymmetric beryllium injector were explored experimentally, using the small-angle X-ray scattering (SAXS) technique available at the Argonne National Laboratory, and numerically, using a homogeneous nucleation model that accounts for droplet temperature variations. Scattering intensity, measured from both inside and outside the injector, was modeled to derive droplet size and liquid volume fraction. The measurement shows that homogeneous nucleation takes place within a narrow spatial region around the nozzle exit for conditions tested. The droplet size reaches the maximum value within the free-jet region. An abrupt decrease in the average droplet size across the Mach disc was observed. The line-of-sight liquid volume fraction decays exponentially with the axial distance from the nozzle exit. Computational predictions indicate reasonable agreement with experimental measurements of average droplet diameter and volume fraction in the free-jet expansion zone. Droplet evaporation downstream of the Mach disk is enhanced in the computational predictions, relative to the experimental data, and within the nozzle, the computational model predicts significant droplet growth via condensation. In contrast, experimental droplet-size distributions indicate that droplet nucleation is the dominant growth mechanism and that growth due to molecular condensation is delayed until the flow exits the nozzle.

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INTRODUCTION

Injection of supercritical fuel has become an increasingly important research area in the development of advanced air-breathing propulsion systems. In some applications, the use of endothermic hydrocarbon fuels as the primary coolant around airframe and combustor components inevitably creates thermally cracked hydrocarbon mixtures at supercritical conditions. The global structures of supercritical jets injected into a quiescent environment have been explored by Lin et al. and Wu et al., using shadowgraph images and Raman scattering. The effects of injection conditions on the global appearance of the jets were characterized and the distribution profiles of the injected species at downstream locations were explored in these studies. It was found that the condensed phase can be generated through the homogeneous nucleation process within the supercritical jets at injection conditions close to the thermodynamic critical state. Injection of the condensed phase can potentially impact the combustion behavior of the engine, due to liquid generation through homogeneous nucleation processes.

Further understanding of droplet nucleation and liquid condensation processes in the injection of supercritical fluid was, however, limited by the capabilities of conventional diagnostic techniques. Recently, properties of the condensed phase within the supercritical ethylene jets, including droplet size and liquid volume fraction, were explored by Lin et al., using the small angle X-ray scattering (SAXS) facility at the Argonne National Laboratory. It was found that the SAXS technique is capable of measuring droplet size and liquid contents inside a highly dynamic condensed jet. The droplet size inside a condensed supercritical ethylene jet is on the order of 50-2000 Å (50-200 nm), which is smaller than that generated from industrial atomizers.

The SAXS technique was then applied to identify the onset of nucleation processes and to characterize droplet properties and liquid contents inside the injector. A 0.5 mm axisymmetric injector made out of beryllium, which allows high X-ray transmittance, was successfully used for the study of internal flow structures of supercritical ethylene jets. Small scatterers on the order of 10-30 Å (1-3 nm) were observed within the injector. The creation processes and identity of these small scatterers, however, could not be confirmed in this study. Detailed probing of the discharged ethylene jets outside the injector and quantitative measurement of the droplet volume fraction, however, were not carried out.

The availability of the quantitative data sets provides an opportunity to validate existing computational models for droplet nucleation/growth process and to assess assumptions used in their formulation. The nucleation/growth model of Ref. differs from that of Ref. in its inclusion of a coupled equation for the droplet temperature. This modification was found necessary to reduce free-jet condensation rates so that the predicted average droplet sizes were more in accord with experiment. Model validation for droplet nucleation process, however, could not be made due to the lack of experimental data.

The objectives of the present study, therefore, are to expand the work of Lin et al. to probe an extended region outside the same beryllium injector and also to explore the effects of internal injector contour on droplet nucleation/growth, using different beryllium injector designs. In this paper, the model of Ref. is further enhanced by the addition of a correlation for self-diffusivity of ethylene, improved vapor-liquid equilibrium predictions near the critical point, and alternative nucleation-rate models valid for high-pressure nucleation processes. Results are compared with the present experimental SAXS data, and directions for future model development are outlined.

EXPERIMENTAL METHODS

Apparatus

The experiment was conducted at the 12-ID-B beamline at Argonne National Laboratory. Pure ethylene (99.5%) at the desired temperature and pressure was injected into a chamber filled with nitrogen. The apparatus consists of an accumulator, a heating/chilling unit, a section of heat exchange tube, a solenoid valve, an injector, and the injection chamber. The chamber is equipped with two mica windows opposite to each other to provide high x-ray transmittance, and two conventional optical windows to allow for visual observation of injection.

The injection chamber is connected to a large injection tank. The injection tank is then connected to the exhaust system through a Venturi vacuum pump to quickly minimize the pressure rise during the injection process. An increase in chamber pressure of less than 10% was observed over the course of injection. Figure 1 shows the integration of the injection chamber setup with the X-ray beamline and detector. The injection chamber was rigidly mounted on a translation stage to provide the desired movement perpendicular to the X-ray for SAXS measurements.

Injection Nozzle

An axisymmetric injector made out of S65C beryllium was used in the present study. Beryllium was selected as the injector material due to its high X-ray transmittance. Figure 2 shows the internal geometry of the beryllium injector. The injector begins with a 7.0 mm diameter passage, followed by a short 43.6° converging section, before reaching a 5.0 mm diameter passage. A second converging section with a converging angle of 120 degrees leads to the final
passage. The final passage has a length 4 mm and a small converging angle of 2 degrees, in order to ensure that the choke point can only occur at the nozzle exit plane. The exit orifice diameter is 1.0 mm. The beryllium injector was placed inside a specially designed protective sleeve, which accommodates three small openings for X-ray access, scattered photon detection, and ethylene discharge. The protective sleeve was installed to minimize the probability of breakage of the mica windows by beryllium fragments in the event of injector failure.

Injection Procedures

In test preparations, the well-purged and evacuated accumulator was first filled with ethylene. The filled accumulator was then pressurized using nitrogen to 5.11 MPa (744 psia), which is greater than the critical pressure of pure ethylene, $P_c = 5.04$ MPa (733.54 psia). Ethylene was then introduced into the heat exchanger to gradually reach the desired injection temperature. For the present study, the injection temperature was maintained at 286.6 K. The critical temperature for ethylene is $T_c = 282.4$ K.

Before injection was initiated, the injection chamber was flushed with nitrogen to remove oxygen for safety concerns and then pressurized with nitrogen to 137 kPa (20 psia). Once the test fluid reached 286.6 K, a solenoid valve was opened for 10 s to discharge ethylene into the injection chamber. Because of the transient behavior of the jet, data obtained during the first 2-3 seconds of injection were discarded. Photo of the ethylene jet is shown in Fig. 3 to illustrate the degree of condensation within the discharged plume.

Instrumentation and Data Reduction

A monochromatic, $0.2 \times 0.2$ mm$^2$ X-ray beam, having a photon flux of $~10^{11}$ s$^{-1}$ in the 12-ID-B beamline, was directed through the injection chamber. The distance between the injector axis and the detector was maintained at 2.0 meters. A photon-counting 2-D array X-ray detector (PILATUS 2M detector) was utilized to capture the forward-scattered X-ray photons. A total of 14 images were obtained for each injection condition. Each image has an integration time of 1.0 second to capture a sufficient number of photons scattered from the medium of interest, which include droplets and precursors of droplet nuclei within the ethylene flow. Scattering signals from the beryllium injector, mica window, and ambient gases were subtracted out.

Figure 4 illustrates the X-ray probing regions associated with specific flow structures and droplet dynamics. In the present study, Zone 1 was designated as the region upstream of the final passage of the nozzle. Zone 2 is the region within the final passage. Zone 3 is the region between the nozzle exit and the Mach disk. Within this zone, fluid is either in the region completely bounded by the circumferential barrel shock and the Mach disk perpendicular to the injector axis or in the region outside the barrel shock. For the present injection condition, the location of the Mach disk is located at $x/d=4$, as predicted by the correlation developed by Crist et al.$^{11}$ and the measurements to be presented later. Zone 4 is the region downstream of the Mach disk. In the present study, the region between $x=-7.0$ mm and $x=13.0$ mm, with $x=0$ at the injector exit, was probed.

Details on data reduction can be found in Ref. [6]. The parameters of interest here are highlighted here. The maximum particle size to which SAXS measurements are sensitive depends on the minimum Q value, with the relationship $D_{max}=2\pi/Q_{min}$. The scattering vector $Q=(4\pi/\lambda\sin(\theta/2))$ ranges from 0.004 Å$^{-1}$ to 0.4 Å$^{-1}$, where $\theta$ is the scattering angle and $\lambda$ is the wavelength. Based on this relationship, the upper detection limit for the maximum diameter is 1570 Å (157 nm) for the present SAXS setup.

The average volume fraction of condensed droplets across the ethylene jet could be computed by integrating the droplet volume distribution with local densities. These densities, however, were not measured in the present study and change throughout the injection processes. In the present study, the liquid volume fraction was calculated with a constant liquid ethylene density of 0.58 g/cm$^3$, based on the study of Edwards et al.$^9$ This value is an adjustment from the value of 0.45 g/cm$^3$ used in Ref. [6].

**NUMERICAL FORMULATION:**

**Supercritical Ethylene Condensation Model**

The computational model is a modified version of that presented in Ref. [10]. The Peng-Robinson equation of state [12]

$$p = Z(\tilde{\rho}, T) \tilde{\rho} R_\gamma T,$$

$$Z(\tilde{\rho}, T) = \frac{1}{1-b\tilde{\rho}} \frac{\tilde{\rho}}{R T (1+2b\tilde{\rho}-(b\tilde{\rho})^2)}$$

(1)

is used to provide local values of the liquid and vapor density and enthalpy, given the pressure and temperature. Here, $\tilde{\rho}$ is the molar density, $R_\gamma$ is the universal gas constant, and $a(T)$ and $b$ are constants and functions that are specific to the substance of interest. The nucleation/growth model considered in this work solves for the total droplet number density and the mass fraction of the vapor phase. Equations for the number density of droplets and the mass density of droplets are formulated as follows:

$$\frac{\partial n}{\partial t} + \frac{\partial (nu_j)}{\partial x_j} = f + \frac{\partial n}{\partial t}

\text{number density}$$

(2)

and
\[
\frac{\partial (\rho Y_i)}{\partial t} + \frac{\partial (\rho Y_i u_j)}{\partial x_j} = \frac{M_n}{N} (g I + nF),
\]
(vapor mass density)
\[(3)\]
with the number of molecules in a critical nucleus given by
\[
g^* = \frac{32\mu}{3} \left( \frac{\sigma(v')}{k_B T} \right)^{\frac{1}{3}} \left( \ln(f'/f_{eq}) \right)^{\frac{1}{3}}, \quad (4)
\]
where \(v'\) is the volume of an ethylene molecule in its liquid state at the local temperature and pressure. The nucleation rate is defined as
\[
I = \frac{2\sigma}{\pi \rho \rho_s^2} \rho_c \exp \left\{ -\frac{16\pi \sigma^2 (v')^2}{3 (k_B T)^2} \frac{1}{\ln(f'/f_{eq})^2} \right\}
\]
where the supersaturation is defined in terms of the vapor-phase fugacity, expressed for the Peng-Robinson EOS as
\[
\ln \left( \frac{f}{\rho} \right) = Z - 1 - \ln(Z - B) = \frac{A}{2\sqrt{2}B} \ln \left( \frac{Z + (1 + \sqrt{2})B}{Z + (1 + \sqrt{2})\frac{\beta}{\beta_{eq}}} \right)
\]
\[A = \frac{a(T)p}{(R_T)^2}, \quad B = \frac{b(T)p}{RT}, \quad (6)\]

Two choices for \(\rho^*\) in Eq. (5) are explored in this work. In the first, used in Refs. [9] and [10], \(\rho^*\) is set to its ideal-gas value: \(\rho^* = p/l(R_T)\). In the second, \(\rho^*\) is set to its saturation-state (equilibrium) value, following Ref. [13]: \(\rho^* = \rho^*_{eq}(T)\). As the saturation-state density at near critical conditions will be generally larger than the ideal gas value, the second variant will result in slightly faster nucleation.

The molecular condensation rate is given as
\[
F = 2\pi d D \frac{\alpha_s}{m_v} (\rho^* - \rho^*_{eq}) \left( \frac{1}{1 + 1.71K_c n} + 1.333(K_c)^3 \right)
\]
where \(d\) is the droplet diameter, \(m_v\) is the mass of an ethylene molecule, \(\rho^*\) and \(\rho^*_{eq}\) are the ethylene vapor densities evaluated at the local pressure and temperature and at the equilibrium state assumed at the droplet surface, and \(K_c\) is a Knudsen number defined as
\[
K_c = \frac{2\pi}{\rho_d^2 \sqrt{2mk_B T}}
\]
\[(8)\]
The solution of the number-density and vapor mass-fraction equation can be combined to yield a prediction of the liquid phase volume fraction:
\[
\alpha_l = \frac{\rho(1-Y)}{\rho(l/p,T)}, \quad \frac{1}{\rho} = \frac{Y_c}{\rho^*_{eq}(p,T)} + \frac{1-Y_c}{\rho^*_{eq}(p,T)}
\]
\[(9)\]
and a prediction of the average droplet diameter through the relation
\[
\alpha_l = n \frac{\pi}{6} d^3
\]
\[(10)\]
Other details of basic formulation may be found in Refs. [9] and [10].

The condensation rate is influenced significantly by the local value of the saturated vapor density at the droplet surface. This is a function of a droplet temperature and is obtained by the solution of a droplet energy equation, written as
\[
\frac{dh/(p,T)}{dt} - \frac{1}{\rho^*_{eq}(p,T) m_v} (\rho^*_{eq}(p,T) I) \left( \rho^*/\rho^*_{eq}(T) - \rho^*_{eq}(T) \right)
\]
\[11\]
where \(T_d\) is the droplet temperature. The equilibrium vapor density at the droplet surface \(\rho^*_{eq}\) in Eq. (7)) is specified using the droplet temperature, and upon rapid expansion of the supercritical fluid, the droplet temperature will lag the vapor-phase temperature. This leads to a reduction in the condensation rate. We also consider two different expressions for the diffusivity \(D\). One is obtained from the assumption of a constant Schmidt number: \(\rho^* D = \mu_s / \alpha_s\), where \(\mu_s\) is the viscosity of ethylene \(^{14}\) and the Schmidt number is set to 0.72. The other is obtained from a curve-fit of experimental data for self-diffusivity of ethylene \(^{15}\) and is expressed through the following expressions
\[
D = 1 \times 10^{-6} (A(T) + B(T)\bar{\rho}\ln\bar{\rho} + C(T)\bar{\rho} + E(T)\bar{\rho}^n) / \bar{\rho}
\]
\[A(T) = A_1 T^n \]
\[B(T) = B_1 + B_2 T + B_3 \]
\[C(T) = C_1 + C_2 T + C_3 \]
\[E(T) = D_1 + D_2 T + D_3 T^2 \]
\[\bar{\rho}\]
\[12\]
Here, \(\bar{\rho}\) is the gas-phase molar density in moles/cm\(^3\) and the constants are assigned the following values:
\[
A_1 = 0.045877 \times 10^{-3}, \quad \eta_1 = 1.23132, \quad B_4 = -2.23665 \times 10^{-3}, \quad B_5 = -0.019150,
\]
\[B_1 = 0.87733 \times 10^{-4}, \quad C_1 = -1.62487 \times 10^{-2}, \quad C_2 = 0.056196, \quad C_3 = 0.64143 \times 10^{-4}, \quad D_1 = 0.022595,
\]
\[B_2 = -0.10285 \times 10^{-3}, \quad D_2 = 0.01281 \times 10^{-4}, \quad \eta_2 = 1.3289\]
We also consider a parachor method\cite{16} for estimating the interfacial tension. Here, the interfacial tension is given by
\[ \sigma = \max(\sigma_0, P_c|\rho_l - \rho_v|^{1/4}) \] (13)
where \( P_c = 100.3 \) is the parachor value for ethylene.\cite{16}

The interfacial tension has to be limited to \( \sigma_0 \), avoid numerical anomalies near the critical point. Some effects of the choice of the limiting value are illustrated later. The coagulation term in Eq. (2) is modeled as a sum of that induced by Brownian motion and by turbulence – the effects of this term are confined to the nozzle walls as the turbulence intensity is higher near the walls.

The above formulation depends on values for the saturation-state densities and the vapor pressure. This information can be obtained by equating vapor and liquid fugacities for a range of temperatures below the critical point and solving for the associated pressure (the vapor pressure). A range of 10000 discrete temperature values between 100 K and the critical temperature of 282.34 K was used to develop a table that contains the saturation-state densities, the vapor pressure, the derivative of the vapor pressure with respect to temperature, and the liquid and vapor spinodal pressures and densities. Bilinear interpolation based on the local temperature value is then used to determine these values as necessary in the flow solution. It should be emphasized that the solution of the vapor-liquid equilibrium problem is specific to the Peng-Robinson equation of state and may not precisely represent the actual response of ethylene, particularly near the critical point.

**Discretization and Time Advancement**

The discretization of the inviscid fluxes uses a version of Edwards' Low-Diffusion Flux-Splitting Scheme (LDFSS)\cite{17} that is valid for real fluids undergoing phase transitions.\cite{18,19} The basic first-order method is extended to second-order spatial accuracy through minmod-limited interpolations of the primitive variable vector \( \tilde{V} = \{ Y_{c,H_4}, Y_r, p, u, v, w, h, k, \omega, n, h_j \} \) to form left- and right states at mesh-cell interfaces. The Menter SST turbulence model is used to provide the eddy viscosity field. Viscous and diffusive components of the equation system are discretized using second-order central differencing techniques. Time integration is facilitated by a planar relaxation method. The code is parallelized using domain-decomposition/MPI message-passing methods.

**Computational Grids and Boundary Conditions**

Axi-symmetric flow is assumed in the calculations. Two meshes, one containing 160×48 cells interior to the nozzle and 216×144 cells exterior to the nozzle and the other containing 160×72 cells interior to the nozzle and 216×216 cells exterior to the nozzle, are used. At the ethylene jet inflow, the stagnation pressure and temperature of the fluid is fixed to the reservoir conditions, and the velocity is extrapolated from the interior. No-slip, adiabatic wall conditions are specified on all solid surfaces. The far-field boundary condition fixes the pressure to the injection chamber value, and all other variables are extrapolated.

**RESULTS AND DISCUSSION**

**SAXS Measurements**

Examination of the scattering intensity profiles from the SAXS measurements is a simple and qualitative way to explore the structures of condensed phase within the flow. Figure 5 shows the selected line-of-sight scattering intensity profiles along the injector axis at different zones. At \( x=6 \) mm in Zone 1, the intensity profile is fairly flat over a wide range of \( Q \) vector, indicating the absence of big scatterers. As the fluid enters the final passage at \( x=2 \) mm (Zone 2), the characteristic scattering intensity profile is similar to the one at \( x=6 \) mm. Only small scatterers exist at this probing location. The lower scattering intensity may be due to a shorter chord length within the flow passage or a reduced concentration of the condensed phase. Once the ethylene exits the injector, scattering characteristics with a negative slope in the logarithm plot can be observed at both locations outside the injector in Fig. 5. The distinct difference in scattering intensity profiles between \( x=2 \) mm (Zone 2) and \( x=6 \) mm (Zone 3) indicates that big scatterers are mainly distributed outside the injector. The wavy scattering intensity profile at \( x=2 \) mm is a classic sign of scattering from big scatterers with their sizes falling within the present SAXS detection limit. The differences in the characteristics of scattering intensity profiles between \( x=2 \) mm (Zone 3) and \( x=6 \) mm (Zone 4, downstream of the Mach disk) indicate the change in scatterer size due to the presence of the Mach disk.

Figure 6 shows the modeling of the scattering intensity profiles to quantify the size of the detected scatterers. Small scatterers on the order of 20 Å (2 nm) were obtained at the \( x=-2 \) and \( -2 \) locations in Figs. 6(a) and 6(b), respectively. The size distribution is fairly monodispersed. As discussed in the study of Lin et al.,\cite{8} creation mechanisms for and identity of these small scatterers could not be confirmed at this stage. They could be aggregates of ethylene molecules at supercritical state, nuclei of ethylene droplets, or even incipient ethylene droplets. At the \( x=2 \) mm location outside the injector, the modeled droplet size is no longer monodispersed. Instead, scatterer sizes between 120 Å (12 nm) and 1800 Å (180 nm) were obtained and are shown in Fig. 6(c). With the present line-of-sight probing, it is impossible to distinguish whether these
big scatterers are distributed within the region bounded the shock structure or outside the barrel shock at this axial location.

The modeled droplet size distribution profile at the x=6 mm location (Zone 4) in Fig. 6(d) is very similar to that at the x=2 mm location (Zone 3) in Fig. 6(c), although the liquid volume fraction is reduced and no scatterers larger than 1100 Å (110 nm) are found.

Line-of-sight averaged droplet size and liquid volume fraction along the injector axis are shown in Fig. 7(a) and Fig. 7(b), respectively. Also shown in Fig. 7 is the axial location of the Mach disk within the injected ethylene plume. The Mach disk is shrouded by the condensed phase. Its location in Fig. 7 is based on prediction from the correlation developed by Crist et al.,11 along with the relevant injection conditions. The prediction of x/d ≈ 4.0 (or x ≈ 4.0 mm) agrees well with the axial location outside the injector, where an abrupt change in the average droplet size can be easily indentified in Fig. 7(a). The abrupt decrease in droplet size is caused by the presence of the Mach disk, which rapidly elevates the fluid temperature for fast droplet evaporation.

An abrupt change in the average droplet size is also found at the injector exit. Inside the injector, the measured scatterer size is fairly constant, on the order of 20 Å (2 nm). Droplets with an average size greater than 600 Å (60 nm) are mainly distributed outside the injector. Based on this observation, the homogeneous nucleation should take place within a fairly narrow spatial region around the nozzle exit, if the 20 Å (2 nm) smaller scatterers are not treated as incipient droplets. For these smaller scatterers to be considered as incipient droplets, the nucleation process would have to start at a location further upstream of the present SAXS probing region, i.e. x < 7 mm. After the nucleation around the nozzle exit, droplet size increases rapidly to reach the maximum size of 1160 Å (116 nm) around x=2 mm in Zone 3. Droplet size then decreases continuously before reaching the Mach disk at x ≈ 4 mm. An abrupt decrease in droplet size across the Mach disk is then observed. The average droplet size of 560 Å (56 nm) is measured immediately behind the Mach disk, followed by a slight increase in droplet size within a short distance before reaching a constant droplet size of around 640 Å (64 nm) for the remaining probing region of the ethylene plume.

Figure 7(b) shows that the calculated line-of-sight liquid volume fraction inside the injector is significantly higher than that outside the injector. If the high liquid volume fraction inside the injector was modeled accurately, the droplet nucleation process must actually take place upstream of the convergent section of the injector to generate the 20 Å (2 nm) small scatterers. In this case, the reduction in liquid volume fraction and the increase in scatterer size at the nozzle exit cannot be reasonably explained. As stated in the Data Reduction section, a constant liquid ethylene density of 0.58 g/cm³ was utilized for the liquid volume fraction modeling in the present study. If the saturated liquid ethylene density of 0.29 g/cm³ at 280K and 4.78 MPa from NIST Chemistry WebBook10 is used for size modeling inside the injector, the derived liquid volume fractions are close to three times higher than the present modeled values. Use of a liquid ethylene density greater than 0.58 g/cm³ inside the injector does not make sense, since the fluid should be closer to the thermodynamic critical state, with a density lower than the liquid ethylene density at a room temperature. With the fluid close to the critical state, the surface tension decreases and the interface between liquid and gas phases can become indistinguishable. Nonetheless, the scattering intensity profiles obtained in the present study clearly indicate the presence of small scatterers. The possibility that the present SANS diagnostics may have captured unique scattering characteristics from the fluid close to the thermodynamic critical state inside the injector cannot be ruled out.

Neglecting the modeled liquid volume fraction inside the injector in Fig. 8(b), the present study indicates that the liquid concentration decreases continuously with an exponential decay rate with the axial distance from the nozzle exit. There is no abrupt change in liquid concentration across the Mach disk, even though the flow condition downstream of the Mach disk promotes droplet evaporation. Also, the increase in droplet size between x=0 and x=2 mm does not result in an increase in liquid volume fraction. Liquid volume fraction less than 10^-4 is not reported in Fig. 8(b), since it is below the accuracy limit of the present modeling efforts.

Radial distribution profiles of the line-of-sight averaged droplet diameter and liquid volume fraction at selected axial locations are shown in Fig. 8 (a) and Fig. 8(b), respectively. Ignoring the radial distribution profiles inside the injectors, it appears that both radial line-of-sight distribution profiles for droplet size and liquid volume fraction exhibit higher values at the core region in Zone 3 and are fairly uniform in Zone 4. Due to the limited resolution of X-ray probing, efforts to derive the actual spatial distribution profiles through inversion techniques, such as the Abell inversion, were not carried out in the present study.

**CFD Modeling**

Numerical predictions of the droplet temperature, average droplet size, and liquid volume fraction on the refined mesh are shown in Fig. 9. The predicted condensation onset occurs within the final passage area (Zone 2) inside the injector. The average droplet diameter is higher near the nozzle wall, probably due to the coagulation effects. In the free jet region, significant
droplet vaporization occurs in the high temperature region immediately behind the Mach disk, resulting in a reduction in the liquid volume fraction. Droplet sizes remain somewhat larger in the shear layer that bypasses the Mach disk but diminish due to evaporation as the ethylene jet mixes with ambient, room-temperature nitrogen gas in the chamber. The liquid volume fraction of condensate quickly increases from the onset of the nucleation process and reaches a peak value of around 0.035 near the end of the nozzle.

Figure 10 presents centerline line-of-sight averages of liquid volume fraction and droplet diameter on the refined mesh. Three models were tested. The ‘baseline’ model utilizes the ideal-gas definition of $\rho$ in defining the nucleation rate and the constant Schmidt-number parameterization of ethylene self-diffusivity and sets the limiting value of the interfacial tension $\sigma_0$ to 0.001. Also included in the comparison is a case in which condensation/evaporation effects are neglected, i.e., nucleation only model. The curve-fit expression for ethylene self-diffusivity is also tested.

In general, the predictions of self-diffusivity from this model are about 50% of the values predicted by the constant Schmidt-number model. The predicted liquid volume fractions within the nozzle are similar to those in the experiment except again, phase separation appears to occur well upstream of the final converging passage in the experiment. The nucleation/growth model greatly over-predicts the average droplet diameter within the nozzle, yielding values greater than 2000 Angstroms which exceeds the SAXS detection limit. The ‘nucleation only’ model again predicts droplet sizes of the order of those measured (25 Angstroms). It appears obvious that condensational growth mechanisms appear to be inhibited within the nozzle. Further downstream, the volume fractions in the free-jet region are again under-predicted, as are the droplet sizes. Rapid evaporation of the droplets downstream of the Mach disk is again indicated in the computational predictions. In the free-jet region, the predictions are more in accord with experimental trends but generally under-predict the measured values. This may indicate either that the free-jet condensation rate is not high enough or that the evaporation rate is too high. The calculation that invokes only nucleation leads to larger volume fractions in the free-jet region and further downstream due to the absence of droplet evaporation mechanisms.

Figure 11 presents line-of-sight averages extracted at different axial locations at various radial stations. These serve to illustrate the spatial variation of the line-of-sight averages. Figure 11(a) shows line-of-sight average droplet sizes at different radial positions. Here, the computational predictions indicate a high degree of radial uniformity in the line-of-sight averages, whereas the experiment indicates that droplet sizes also are larger along lines of sight extending through the centerline. Within the nozzle, agreement with experiment is poor for the nucleation/growth model, as discussed earlier. The effect of incorporating the curve-fitted expression for ethylene self-diffusivity is to reduce the average droplet sizes slightly. Droplet volume-fraction predictions shown in Fig. 11(b) indicate that the peak droplet volume fraction within the free-jet region ($x=2$ mm) occurs near the centerline, as expected. The droplet population diminishes near the edge of the free shear layer. The predicted values are lower than measured at all stations external to the nozzle, but the shapes of the distributions are relatively well-predicted. Within the nozzle, the line-of-sight average volume fraction is nearly independent of radial position, and agreement with experiment is good.

**SUMMARY**

The structures of condensed supercritical ethylene jets injected from an axisymmetric beryllium injector were explored using the small-angle X-ray scattering (SAXS) technique. The experiment was conducted at the 12-ID-B beamline at the Argonne National Laboratory. Beryllium was selected as the injector material, due to its high X-ray transmittance. Scattering intensity was measured both inside and outside the injector and was modeled to derive size and population of scatterers. Properties of droplet size and liquid volume fraction inside the injector and within the ethylene plume were then investigated. The SAXS measurements were used to assess a homogeneous nucleation/growth model based on the Peng-Robinson state equation for ethylene.

The measurements show that small scatterers on the order of 20 Å (2 nm) were modeled from the present measurements inside the injector. With an assumed liquid ethylene density for these small scatterers, unusually high liquid volume fractions were obtained. Identity of these small scatterers could not be confirmed in this study. Neglecting the uncertainties related to the identity and source of the 20 Å (2 nm) small scatterers, homogeneous nucleation takes place within a narrow spatial region around the nozzle exit. The average droplet size is around 700 Å (70 nm) immediately outside the injector and reaches 1200 Å (120 nm) before the Mach disk. An abrupt decrease in the average droplet size across the Mach disk was observed, due to the temperature rise downstream the Mach disk. In the region downstream the Mach disk, the line-of-sight average droplet size is fairly constant. The line-of-sight liquid volume fraction decays exponentially with the axial distance from the nozzle exit. The presence of Mach disk has little if any effect on the continuous decrease in the line-of-sight liquid volume fraction.
The numerical modeling results show that the basic nucleation/growth model, enhanced by including a droplet energy equation and a model for ethylene self-diffusivity, can provide quantitatively correct predictions of condensate volume fraction and average droplet diameter in the free-jet expansion region. The model appears to over-predict the droplet evaporation rate, relative to experimental observations, and predicts rapid growth of droplets due to molecular condensation within the nozzle. In contrast, experimental observations indicate that droplet growth is inhibited within the nozzle though nucleation does occur. The results provided by the computational model appear to be consistent with the thermodynamic state description provided by the Peng-Robinson equation of state, but simplifications such as the assumption of a locally monodisperse droplet size distribution and inaccuracies in the Peng-Robinson state description near the critical point may compromise predictive capability for the initial stages of droplet formation.

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REFERENCES


Figure 1. Photos of experimental setup in 12-ID-B beamline. (a) Setup around injection chamber, (b) detector setup. X-ray is from right to left.

Figure 2. Schematics to illustrate details of axisymmetric beryllium injectors.

Figure 3. Photo of the supercritical ethylene jet injected from the beryllium injector into quiescent chamber.
Figure 4. Schematic to illustrate the X-ray probing regions. 1) Major converging section for Zone 1; 2) final passage section for Zone 2; 3) between the nozzle exit and Mach disk for Zone 3; 4) downstream the Mach disk for Zone 4. The shock structure shown is from a typical gas jet and may be invisible in a heavily condensed jet.

Figure 5. Scattering intensity profiles at various axial locations. r=0.

Figure 6. Modeled size distributions at various axial locations. (a) Zone 1, x= -6.0 mm, (b) Zone 2, x= -2.0 mm, (c) Zone 3, x= 2.0 mm, (d) Zone 4, x= 6.0 mm.
Figure 7. Axial distribution profiles of line-of-sight (a) averaged droplet diameter and (b) liquid volume fraction.

Figure 8. Radial distribution profiles of line-of-sight (a) averaged droplet diameter and (b) liquid volume fraction at various axial locations.
Figure 9. Numerically predicted contours for droplet temperature, droplet diameter, and liquid volume fraction.

Figure 10. Centerline line-of-sight predictions of (1) liquid-phase volume fraction and (b) averaged droplet diameter.

Figure 11. Line-of-sight (a) liquid-phase droplet volume fractions and (b) droplet diameter at different radial and axial stations.