An integral multi-phase turbulence compressible jet expansion model for accidental releases from pressurized containments

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The accurate prediction of the conditions of a pressurized jet upon its expansion to atmospheric pressure is of fundamental importance in assessing the consequences associated with accidental releases of hazardous fluids from pressurized containments. An integral multi-phase compressible jet expansion model which for the first time accounts for turbulence generation is presented. Real fluid behavior is accounted for applying a suitable equation of state. Using the accidental release of two-phase CO_2 from a pressurized system as an example, the proposed model is shown to provide far better predictions of the fully expanded jet momentum, and hence its downstream flow characteristics as compared to existing integral models where the impact of turbulence generation is ignored.

Keywords: process safety, multiphase flow, turbulence, jet expansion

1. INTRODUCTION

Over 3.6 million km of pressurized pipelines have been constructed to transport enormous quantities of highly flammable hydrocarbons around the world[1]. Globally, the total length of hydrocarbon transportation pipelines has increased a 100 fold in the past 50 years with over 32,000 km of new pipelines being constructed every year. Despite the fact that pipelines are generally considered to be the safest mode of hydrocarbon transportation, it is estimated that there are an average of 250 pipeline rupture incidents per year, some resulting in catastrophic loss of life, property damage and environmental pollution[2,3]. According to data published by the US Department of Transport[4], even short, simple pipelines will have a reportable accident during a 20 year life time. Operators of long pipelines (1000 km or over) can expect a reportable accident at a frequency of 1 per year.

Ironically, pressurized pipelines are also expected to play a major role in combating the effects of global warming by transporting the captured CO_2 from power plants for subsequent geological sequestration[5]. Notably, some estimates indicate that by 2030 there will be over 100,000 km of CO_2 pipelines carrying millions of tons of CO_2 across the globe[6]. Given that CO_2 at concentrations greater than 10% v/v is asphyxiant, the safety of such pipelines has been the focus of significant attention in recent years[7,8,9].

As part of their safety assessment, the accurate determination of the conditions of the pressurized jet upon its expansion to atmospheric pressure in the event of pipeline failure is of fundamental importance. Such data serves as the source term for determining all the major consequences associated with an accidental release including fire, explosion or dispersion of hazardous/toxic clouds thus forming the basis for the safe pipeline routing and emergency response planning.

The mathematical modeling of the transient outflow following pipeline failure may be divided into three sequential components. These include discharge at the rupture plane, which for the most part will be choked, jet expansion to atmospheric pressure followed by far-field dispersion of the merging cloud where air entrainment is expected to be significant. The modeling of discharge at the rupture plane for single- or two-phase fluids has been the subject of a number of studies[8,9,10]. Depending on their level of sophistication in terms of for example accounting for various pertinent phenomena such as heterogeneous flow behavior and phase dependent in-pipe heat transfer and frictional effects, reasonably good agreement with real pipeline rupture data has been reported. Dispersion modeling of escaping buoyant or heavy clouds on the other hand is a mature subject having received considerable attention in the past decades[11,12,13]. However, the analytical modeling of the intermediate stage, *i.e.* the jet expansion to the ambient pressure is often based on simplistic physical approximations such as isenthalpic or isentropic jet expansion immediately downstream of the rupture plane[14,15]. This is a considerable drawback given that the predicted fully expanded conditions form the boundary conditions needed for the downstream dispersion simulation. The importance of the correct modeling of the jet expansion was clearly demonstrated in a study of the dispersion behavior of a flashing jet by Calay and Holdo[16] using CO_2 as the working fluid.

In recent years, a number of robust Computational Fluid Dynamic (CFD) models, successfully resolving the flow field of expanding jets accounting for phase change, turbulence effects and shock formation have been developed.

Liu *et al.*[17] for example conducted CFD simulations for highly under-expanded single-phase CO_2 jets, applying the Peng-Robinson (PR) Equation of State (EoS)[18] to account for real gas behavior. The predicted fully expanded conditions were subsequently used as the boundary conditions for dispersion modeling, obtaining good agreement with the recorded downstream CO_2 concentration experimental data.

In the case of dense-phase CO_2 (*i.e.* pressure higher than 74 bar), widely considered to be the most economical way of its pipeline transportation[19], the transition below the triple point (216.6 K, 5.18 bar[20]) leading to solid CO_2 formation is likely following accidental rupture. The possibility of solid formation is of concern given that the subsequent delay in its sublimation impacts the CO_2 cloud dispersion hazard profile. To accout for CO_2 liquid/solid transition, a composite EoS was proposed by Wareing *et al.*[21]. This EoS was later implemented in their CFD model for jet expansion and subsequent near-field dispersion[22]. The flow was assumed to be homogeneous and a thermodynamic relaxation model was applied to account for the delay in the sublimation of solid CO_2. As part of the CO2QUEST[23] and CO2PipeHaz[24] EU-funded projects, the present authors successfully validated their model based on comparisons of the measured near-field CO_2 temperatures and concentrations following the rupture of a fully instrumented 40 m long, 0.5 m internal diameter dense-phase CO_2 pipeline[25].

To account for the effects of solid phase CO_2 particle dynamics on the dispersion behavior following pipeline failures, Gant *et al.* [26] used the fully expanded flow conditions predicted from a multiphase CFD model as the boundary conditions for their atmospheric dispersion model with Lagrangian particle tracking method. Relatively good agreement with the recorded experimental data for the downstream CO_2 concentrations and temperatures was obtained.

Despite their success, a major practical drawback associated with the use of expanded jet CFD models is the heavy computational workloads required to produce accurate simulations. This severely restricts their application when performing routine pipeline safety assessment. In such cases, by necessity multiple accidental release scenarios based on generic puncture diameters up to full bore rupture will be required at various locations along the pipeline, particularly near populated areas. This will be even more problematic in the case of long pipelines (*e.g.* > 300 km) where computational run times will become prohibitive.

Liu *et al.*[17]for example, showed that discretizing the computational domain into 0.49 million cells and using a time step size of 1.0×10^{-7} s was necessary to resolve the flow field of jet expansion while maintaining solver convergence. In their study of highly-turbulent under-expanded hydrogen and methane jets, Hamzehloo and Aleiferis[27] on the other hand showed that an even smaller time step of 5.0×10^{-9} s was required in order to produce reasonably accurate predictions of large pressure gradients in the flow close to the discharge orifice. Other relevant studies include the impact of changing back pressure on shock stability by Irie *et al.*[28] and the Large Eddy Simulation of stable supersonic jets by Dauptain *et al.*[29], both reported high computational demand to resolve the rapid transients.

To address the heavy computational workloads associated with the CFD models, simple quasi-one-dimensional jet expansion models have been developed. In particular, the steady one-dimensional flow analytical jet expansion model developed by Le Martelot *et al.*[30] deals with multi-phase flows by using the Stiffened Gas EoS (SG-EoS)[31] and assuming homogenous equilibrium between the constituent fluid phases. However, this model is designed for confined flows in known geometries and hence not suitable for unconfined jets formed during accidental releases from pressurized pipelines.

In their study of a two-phase jet close to a puncture based on homogeneous equilibrium and isentropic assumptions, Vandroux-Koenig and Berthoud[32] considered the behavior of the jet fragmentation due to flashing. An over-prediction of the velocity at full expansion was found compared to the measured data.

More complete jet expansion integral models based on the conservation laws accounting for the inventible change in entropy and fluid acceleration, have been developed to provide the source term for the downstream dispersion modeling [33,34,35].

The so far reported integral models neglect both viscous dissipation and turbulence effects. The net loss or gain of the jet's mean bulk kinetic energy is the sum of pressure work, work done by viscous stress (*i.e.* viscous dissipation) and energy exchange between the mean bulk flow and the associated turbulence motions[36,37]. Although for most flows, viscous dissipation is relatively small and may be ignored, the potential error introduced by ignoring turbulence generation is uncertain. As the high-speed jet penetrates the surrounding air, turbulences at the jet boundary are produced. The kinetic energy of these turbulent motions, also known as the turbulent kinetic energy, is taken directly from the mean bulk flow. This leads to a loss of the mean bulk flow kinetic energy, which may be significant and should therefore be considered.

This work presents the development and testing of a computationally efficient integral multi-phase jet expansion model based on the solution of mass, momentum and energy conservation equations, which takes into account turbulence generation. Real fluid behavior is accounted for using a suitable equation of state. Using the accidental release of two-phase CO_2 following the puncture of a high pressure containment as a working example, the integral model's performance is evaluated by comparisons of its predictions against a rigorous but computationally demanding turbulent jet CFD model. The importance of turbulence generation is demonstrated by comparing the model predictions against those obtained where its effect is ignored.

2. METHOD

2.1 Integral jet expansion model. In this study, the emerging two-phase CO_2 jet is assumed to be at thermodynamic and mechanical equilibrium within its constituent phases. Furthermore, air entrainment is assumed to be negligible in the jet expansion region prior to its pressure equilibration with the surrounding ambient.

Given the above, the conservation of mass, momentum and energy of the expanding jet can be written as follows[35]:

$$\overline{\rho}_1 \overline{U}_1 A_1 = \overline{\rho}_2 \overline{U}_2 A_2 \tag{1}$$

$$-\overline{\rho}_1 \overline{U}_1 A_1 \overline{U}_1 + \overline{\rho}_2 \overline{U}_2 A_2 \overline{U}_2 = A_1\left(\overline{p}_1 - \overline{p}_2\right) \tag{2}$$

$$\overline{h}_1 + \overline{U}_1^2/2 = \overline{h}_2 + \overline{U}_2^2/2 \tag{3}$$

where $\overline{U}$ and A are the mean velocity and cross-section area of the expanding jet. $\overline{p}$, $\overline{\rho}$ and $\overline{h}$ are the corresponding mean pressure, density and enthalpy respectively. The subscripts 1 and 2 stand for the locations at the rupture plane and in the fully expanded jet. Solving the above algebraic system together with the Extended Peng-Robinson (EPR) EoS[38], the fully expanded jet conditions including its density, enthalpy, velocity and area are obtained without considering the viscous dissipation and the turbulence generation.

However, as stated in Introduction, turbulence generation may lead to losses in the mean bulk flow kinetic energy. To account for such effect, an additional term, k_t representing the corresponding turbulent kinetic energy following expansion to ambient pressure is added to equation (3). The resulting energy conservation is given by:

$$\overline{h}_1 + \overline{U}_1^2/2 = \overline{h}_2 + \overline{U}_2^2/2 + k_t \tag{4}$$

Adequate modeling is required for k_t; In order to express k_t in terms of $\overline{U}_2$, we utilized the logarithmic velocity profile in the flow obtained from the solution of the k-ε turbulence model assuming constant pressure and shear stress across the jet following Richards and Hoxey[39]. In this case, k_t is expressed as:

$$k_t = \frac{u_\tau^2}{\sqrt{C_\mu}} \tag{5}$$

where, C_μ is the model constant (C_μ = 0.09) and u_τ is the friction velocity which characterizes the logarithmic velocity profile of the flow:

$$u(r) = \frac{u_\tau}{\kappa} \ln\left(\frac{r + r_0}{r_0}\right) \tag{6}$$

where, κ and r_0 are the Von Karman constant (κ = 0.41) and the aerodynamic surface roughness length (r_0 = 0.0015), respectively[40].

Integrating equation (6) across the jet gives an expression relating the average velocity at full expansion, $\overline{U}_2$ and the friction velocity, u_τ:

$$\overline{U}_2 = \frac{u_\tau}{\kappa \pi R_2^2} \int_{R_2}^{0} \left[\ln\left(\frac{r + r_0}{r_0}\right) \pi r \right] dr \tag{7}$$

Rearranging equation (7) for u_τ and substituting into equation (5) gives:

$$k_t = \frac{1}{\sqrt{C_\mu}} \left(\frac{\overline{U}_2 \kappa \pi R_2^2}{\int_{R_2}^{0} \ln(r + r_0/r_0) \pi r dr} \right) \tag{8}$$

Given that viscous dissipation (*i.e.* the conversion of kinetic energy to the internal energy) is negligible compared to turbulent kinetic energy production[36,37], the enthalpy at full expansion, $\overline{h}_2$ can be expected to be the same as that predicted by solving equation (1) to (3). In order to correct the fully expanded jet velocity, $\overline{U}_2$ and area, A_2, equations (1), (4) and (8) are solved numerically using a non-linear algebraic solver in Matlab.

2.2 CFD jet expansion model. In order to test the performance of the Integral Jet Expansion Model (IJEM) and Integral Jet Expansion Model with Turbulence (IJEM-T), their model predictions are compared to a rigorous CFD jet expansion model which resolves the key jet expansion physical phenomena, including the phase change, formation of shocks prior to full expansion and turbulence effects.

The following describes the governing equations of the flow field during jet expansion and the turbulence model used in this study. The pertinent thermodynamic properties of the CO_2 jet are predicted using the EPR-EoS while that of the surrounding air are described by the standard PR-EoS.

2.2.1 Governing equations. The compressible Reynolds-Average Navier-Stokes multiphase mixture model is used to describe the mechanics of the flow. The resulting mass, momentum and energy conservation equations based on the homogenous equilibrium assumption are respectively given by:

$$\frac{\partial}{\partial t}\bar{\rho}+\frac{\partial}{\partial x_i}\left(\bar{\rho}\bar{U}_i\right)=0 \tag{9}$$

$$\begin{aligned}&\frac{\partial}{\partial t}\left(\bar{\rho}\bar{U}_i\right)+\frac{\partial}{\partial x_i}\left[\bar{\rho}\bar{U}_i\bar{U}_j\right]\\&+\frac{\partial}{\partial x_i}\left[-\bar{\rho}\overline{u_i^{'}u_j^{'}}-\mu\left(\frac{\partial\bar{U}_i}{\partial x_j}+\frac{\partial\bar{U}_j}{\partial x_i}\right)+\bar{p}\right]=0\end{aligned} \tag{10}$$

$$\begin{aligned}&\frac{\partial}{\partial t}\bar{E}+\frac{\partial}{\partial x_i}\left[\left(\bar{E}+\bar{p}\right)\bar{U}_i-\bar{U}_i\overline{u_i^{'}u_j^{'}}\right]\\&-\frac{\partial}{\partial x_i}\left(\lambda\frac{\partial\bar{T}}{\partial x_i}\right)+S_E=0\end{aligned} \tag{11}$$

where $\bar{\rho}$, $\bar{p}$ and $\bar{T}$ are the mixture mean density, pressure and temperature respectively. $\bar{E}$ is the mixture mean total energy ($\bar{E}=\bar{h}-\bar{p}/\bar{\rho}+\bar{U}^2/2$). λ and μ are the conductivity and viscosity of the mixture respectively. $\overline{u_i^{'}u_j^{'}}$ is the Reynolds stress tensor. S_E is the volumetric heat production source term. The governing equations are solved in ANSYS Fluent 14.0 using a pressure-based implicit scheme[41].

2.2.2 Turbulence modeling. In order to provide closure to the Reynolds stress tensor, $\overline{u_i^{'}u_j^{'}}$ in equations (10) and (11), turbulent viscosity models are selected. According to the Boussinesq eddy viscosity assumption, the Reynolds stress tensor is proportional to the trace-less mean strain rate tensor, $\overline{S}_{i,j}$ [36]:

$$\overline{u_i^{'}u_j^{'}} = -\left(\frac{2\mu_t \overline{S}_{i,j}}{\rho} - \frac{2}{3}k\delta_{ij}\right) = -\frac{\mu_t}{\overline{\rho}}\left(\frac{\partial \overline{U}_i}{\partial x_j} + \frac{\partial \overline{U}_j}{\partial x_i}\right) - \frac{2}{3}k\delta_{ij} \tag{12}$$

where μ_t is the turbulent viscosity. Amongst various turbulent viscosity models, two-equation models are chosen over less complex ones such as the mixing-length model because of the difficulties in specifying the algebraic mixing length scale for external flows (*i.e.* jet expansion). There are several well-established two-equation models, such as the *k-ε* model, the *k-ω* model and the *k-ω* Shear Stress Transport (SST) model[42]. In comparison with the *k-ε* model, the standard *k-ω* model has the advantage of correctly predicting the turbulences in boundary layers (*e.g.* near solid boundaries) and adverse pressure gradients generated during flow separation. However, the standard *k-ω* model is very sensitive to specific dissipation rate *ω* specified at the flow boundaries, which makes it less applicable to free stream flows. On the other hand, the *k-ω* SST formulation, combines features of both the *k-ω* and the *k-ε* models, and has the capability of accurately predicting the turbulences in boundary layers as well as in high Reynolds number free stream flows. The *k-ω* SST model transport equation set is given by:

$$\frac{\partial(\overline{\rho}k)}{\partial t} + \frac{\partial(\overline{\rho}\overline{U}_i k)}{\partial x_i} = P_k - \beta^*\overline{\rho}k\omega + \frac{\partial}{\partial x_i}\left[(\mu + \sigma_k\mu_t)\frac{\partial k}{\partial x_i}\right] \tag{13}$$

$$\frac{\partial(\bar{\rho}\omega)}{\partial t}+\frac{\partial(\bar{\rho}\bar{U}_i\omega)}{\partial x_i}=P_\omega-\beta\bar{\rho}\omega^2 + 2\bar{\rho}\sigma_{\omega,2}(1-F_1)\frac{1}{\omega}\frac{\partial k}{\partial x_i}\frac{\partial \omega}{\partial x_i} \tag{14}$$

where P_k and P_ω are the effective production rate of turbulent kinetic energy and its specific dissipation respectively. F_1 is the blending function. Each invariant in the SST model (σ_k, σ_ω, β, β^* and α) is calculated by a linear combination of corresponding constants in the k-ε and k-ω models:

$$\sigma_k=(1-F_1)\sigma_{k,1}+F_1\sigma_{k,2} \tag{15}$$

where model constants with subscript 1 and 2 correspond to the k-ω and k-ε model respectively. Consequently, in the close wall region, F_1 takes the value of 1 which corresponds to the standard k-ω formulation; away from wall region, F_1 takes the value of 0, which reduces the transport equation set to the k-ε model.

In addition, modifications of the turbulence transport equations are required to take the fluid compressibility effect, also known as turbulent dilution effect, into account. Following Sarkar *et al.*[43], the turbulent viscosity is related to the turbulent Mach number, $M_t=\sqrt{2k}/c$ (where c stands for local speed of sound) through the relation, $\mu_t=0.09\bar{\rho}k^2/(1+M_t^2)\varepsilon$; a source term $S_k=-\bar{\rho}M_t^2\varepsilon$ is introduced to the RHS of the turbulent kinetic energy transport equation (13).

2.2.3 Computational flow domain and boundary conditions. Figure 1A shows the axisymmetric computation flow domain adopted for simulating the expanding CO_2 jet downstream of the 6 mm diameter, 9 mm long release nozzle. The computational flow domain dimensions are chosen as 200 mm across and 1000 mm long to fully envelop the expanding jet observed in the experiment (Figure 1B).

To close the conservation equations (9), (10) and (11) and the transport equations (13) and (14), the boundary conditions adopted for the flow are specified at the edges of the flow domain (Figure 1A):

(i) Inlet: specified mass flowrate, pressure and temperature and turbulence quantities k and ω. The latter are estimated as[41]:

$$k = \frac{3}{2}(uI)^2 \tag{16}$$

$$\omega = \frac{k^{1/2}}{0.09^{1/4} l} \tag{17}$$

where I and l are respectively the turbulence intensity and the length scale defined as:

$$I = 0.16\,\mathrm{Re}^{-1/8} \tag{18}$$

$$l = 0.07\,D \tag{19}$$

where Re is the Reynolds number and D is the orifice diameter;

(ii) Wall: zero-gradient boundary condition for pressure and temperature. The velocity, k and ω in the cell adjacent to the wall are specified based on the standard wall function;

(iii) Outlet (ambient): zero-gradient boundary condition for all the flow variables;

(iv) Jet axis: symmetry plane boundary condition for all the flow variables.

At time t = 0 s, the entire flow domain is initialized with stagnant air at the ambient conditions corresponding to each test (Table 1).

Table 1: Case study flow conditions; Subscript 0, 'amb' and 1 represent the upstream, ambient and rupture plane conditions respectively.

	Case study no.	T_0 (K)	p_0 (bar)	T_{amb} (K)	p_{amb} (bar)	T_1 (K)	p_1 (bar)	Liquid phase mass fraction
Vapor upstream	1a	264.3	27	272.1	1	246.0	16	0.07
	2a	280.1	44	281.6	1	260.7	25	0.11
	3a	278.1	39	278.1	1	258.5	23	0.10
Liquid upstream	1b	264.3	27	272.1	1	256.3	22	0.94
	2b	280.1	44	281.6	1	271.2	33	0.91
	3b	278.1	39	278.1	1	267.2	30	0.90

Grid sensitivity analysis was carried out and little variance in the results (e.g. axial velocity) was found by increasing the number of grid cells from 0.3 to 0.7 million (see Figure 2). Therefore, the discretized flow domain with 0.3 million cells was adopted for the subsequent simulations. The flow Courant number is set to the recommended value of 5[41] and a typical time step size is 5×10^{-7} s. The convergence criterion is defined as the residual of each flow variable becoming less than 10^{-4}.

2.3 Fluid properties. The required CO_2 phase equilibrium data are obtained using the EPR-EoS capable of handling the phase transition to the solid phase:

$$\bar{p} = \frac{R\bar{T}}{\bar{v}-b} - \frac{a}{\bar{v}(\bar{v}+b)+b(\bar{v}-b)} \tag{20}$$

where v and R are the specific volume and the universal gas constant respectively. a and b are model parameters specific to the vapor-liquid and vapor-solid two-phase mixtures.

For a two-phase mixture at thermal equilibrium, the specific enthalpy of the mixture is given by:

$$\bar{h} = \bar{q}\bar{h}_v + (1-\bar{q})\bar{h}_{l,s} \tag{21}$$

where $\bar{q}$ is the vapor phase mass fraction. Subscripts v, l and s respectively denote the vapor, liquid and solid phases. The mixture density is defined as:

$$\frac{1}{\bar{\rho}} = \bar{q}\frac{1}{\bar{\rho}_v} + (1-\bar{q})\frac{1}{\bar{\rho}_{l,s}} \tag{22}$$

The transition from the CO_2 liquid phase to solid phase across the triple point is modeled using a smoothing approach following Woolley *et al.*[22]:

$$w(T) = [1 - S(T)]w_l(T) + S(T)w_s(T) \tag{23}$$

$$S(T) = 0.5 + 0.5\tanh\left(\frac{T - T_{tr}}{b}\right) \tag{24}$$

where $w(T)$ is the specific property of interest (density or specific enthalpy), $w_l(T)$ and $w_s(T)$ are respectively the properties of the saturated liquid and solid phases. T_{tr} is the CO_2 triple point temperature (216.6 K) and b is the smoothing factor (b = 5).

3. RESULTS AND DISSCUSSIONS

Six case studies involving various release conditions, applying IJEM (Integral Jet Expansion Model), IJEM-T (Integral Jet Expansion Model with Turbulence) and the CFD model (as base case) are carried out to simulate jet expansion.

3.1 Release conditions in the case studies. For the purpose of this study, the release conditions for the high pressure vessel CO_2 release tests conducted by Hébrard *et al.*[44] are selected as test cases for our simulations. In these tests, a 2 m^3 heavily insulated spherical CO_2 tank was connected to a 50.8 mm diameter 6 m very smooth steel pipe incorporating a 9 mm long and 6 mm diameter orifice nozzle at its end. The other end of the pipe terminated at a height of *ca.* 150 cm above the vessel's base. The vessel was initially partly filled with saturated liquid CO_2. Upon instantaneous opening of the orifice using a pneumatically operated valve, approximate steady upstream conditions during the first 120 s of release were observed based on monitoring the mass release rate and the discharge temperature.

The upstream and ambient conditions for each of the six case studies are presented in Table 1. Case studies 1a – 3a are for saturated vapor phase upstream whereas case studies 1b – 3b are for saturated liquid phase upstream. Table 1 also shows the corresponding calculated rupture plane (choked) conditions based on isentropic expansion approximation[45] along with the liquid mass fractions at the nozzle orifice.

3.2 CFD model results. Figure 3 to 6 respectively represents the CFD simulation results for the pressure, temperature, liquid/solid phase mass fraction, and velocity profiles along the jet axis as measured from the release point (the origin) at 1.0 s. Figure 3 also shows the corresponding CFD pressure contour plot presented as an example.

Four distinct trends may be observed in the data presented. In the order of appearance these are: (i) An initial plateau representing the almost constant flow conditions across the 9 mm long nozzle; (ii) The inflection points (*ca.* 15 mm downstream of the nozzle orifice) for the jet temperature and pressure. These correspond to the release of the latent heat of fusion associated with the transition through the triple point of CO_2[21]; (iii) Discontinuities corresponding to the location of the Mach shock (*ca.* 30 mm from the puncture plane). It can be noticed that there is a spike in the temperature predictions at the Mach shock location. This is attributed to the second order interpolation scheme adopted in this study which is known to cause numerical oscillations at the flow locations with large gradients; (iv) A second plateau corresponding to jet pressure stabilization at ambient pressure (1.0 bar). At this point, the jet remains at its sublimation temperature of 194.3 K (see Figure 4) and solid phase CO_2 is present (at mass fraction of *ca.* 0.40, Figure 5).

Figure 7 is the corresponding CFD contour plot for CO_2 mass fraction. As it may be observed, air entrainment only occurs at the jet boundary as most of the jet core is pure CO_2. This supports the validity of negligible air entrainment assumption employed in the integral jet expansion model.

Figure 8 to 10 respectively represents the corresponding CFD model generated cross-section radial profiles (solid lines) for the fully expanded jet momentum flux, temperature and density (*ca.* 30 mm from the rupture plane). The plots' origins represent the jet centers. Additionally, in order to enable quantitative comparisons between the CFD and the integral model predictions, the representative integrated averages are presented by the dotted lines. The cut off points (dotted vertical lines) represent the locations of the jet/air boundaries; they are determined by conserving the discharge mass flowrate.

It is interesting to note the larger size of the expanded jet radius in the case of the liquid CO_2 upstream as compared to the vapor upstream (*cf.* Figure 8A and Figure 8B). Also, as expected the jet radius increases with an increase in the upstream pressure.

Referring to the temperature plots (Figure 9) as it may be observed, in all cases the jet temperature remains constant at the CO_2 sublimation temperature (194.3 K) across its radius. The crossing of the expanded jet boundary is marked by a rapid rise in temperature due to the mixing with surrounding warmer air.

Turning to Figure 10B, as expected in the case of the liquid upstream scenarios, a rapid drop in the density is observed on crossing the jet boundary due to the mixing with less dense surrounding air. The above trends are far less dramatic in the case of the vapor upstream (Figure

10A) due to its similar density at full expansion as compared to the surrounding air. The predicted higher density near the interior of the jet cross-section in case study 1b is due to its higher CO_2 solid phase mass fraction as compared to the other case studies.

3.3 Integral model results. Table 2 represents the jet temperature, CO_2 solid phase mass fraction, jet radius and momentum flux predictions for all the test scenarios as predicted by IJEM. In order to demonstrate the impact of turbulence generation, the momentum flux predictions by IJEM-T are also presented. Given that both integral models ignore any dissipation, for the same case study only one set of thermodynamic data (temperature and CO_2 solid phase fraction) is presented.

Table 2: Fully expanded jet conditions (at ambient pressure).

	Case study no.	Temperature (K)	Solid phase mass fraction	Radius (IJEM) (m)	Radius (IJEM-T) (m)	Momentum flux (IJEM) (kg/m-s^2)	Momentum flux (IJEM-T) (kg/m-s^2)
Vapor upstream	1a	194.3	0.08	0.0084	0.0097	4.13×10^5	1.99×10^5
	2a	194.3	0.10	0.011	0.013	4.04×10^5	2.12×10^5
	3a	194.3	0.09	0.010	0.012	4.08×10^5	2.11×10^5
Liquid upstream	1b	194.3	0.40	0.017	0.019	0.91×10^5	0.51×10^5
	2b	194.3	0.35	0.019	0.022	1.19×10^5	0.70×10^5
	3b	194.3	0.36	0.018	0.021	1.21×10^5	0.69×10^5

As it may be observed, the same trends in the data as compared to the CFD predictions described above are obtained. The fully expanded jet temperature corresponds to the CO_2

sublimation temperature (194.3 K). Furthermore, an increase in the upstream pressure is manifested in an increase in the fully expanded jet radius, hence its area.

3.4 Comparison of the model results. Figure 11 to 13 respectively presents the comparisons of IJEM and IJEM-T predictions against the averaged CFD simulation data for the fully expanded jet conditions including the density, internal energy and jet momentum flux. Since thermodynamic predictions are the same for both integral models, only one set of data for these predictions is presented. The 45 degree line is also drawn in each figure to provide a direct measure of the degree of disagreement with the CFD predictions.

Given that the fully expanded jet is at solid/vapor equilibrium, as can be expected, all the three models predict the temperature of the CO_2 jet to be at the sublimation point (194.3 K).

Turning to the density predictions (Figure 11), the maximum percentage difference between the integral models and the CFD models is ± 5%.

Figure 12 shows the comparison of the corresponding internal energy predictions. The reasonably good agreement (± 5 %) between the two models is indicative of the validity of negligible dissipation assumption made in the integral models.

Moving to Figure 13 showing the comparison of the momentum flux predictions from the three models, it is clear that IJEM model grossly over predicts the momentum flux by more than 50%. In the case of IJEM-T, which accounts for turbulence generation, this disagreement is significantly reduced, producing a maximum overestimate of *ca.* 15%. This finding is significant given that the jet momentum dictates the subsequent 'spread' of the dispersing cloud.

4. CONCLUSIONS

Understanding and the accurate modeling of the characteristics of a high pressure jet prior to its full expansion to ambient pressure is pivotal to the proper modeling of its subsequent atmospheric dispersion behavior.

In this work, the development and testing of an integral multi-phase jet expansion model aimed at dealing with the heavy computational workloads associated with CFD models serving the same purpose was presented. In contrast to previous approaches, the integral model for the first time accounted for the inevitable losses in the bulk mean kinetic energy of the expanding jet due to turbulence generation. The verification of the model was based on the comparisons of its predictions against a multiphase CFD jet expansion model accounting for key physics involved including phase change, shock formation and turbulence effects. Due to its rigor, the computational loads associated with the CFD models are usually intensive. This makes it impractical as a tool for routine safety assessment of the consequences associated with accidental releases form high pressure containments.

The verification tests involved a series of realistic case studies for the high pressure releases of gaseous and liquid phase CO_2 from a pressurized storage tank discharging through a nozzle. Our previously developed EPR-EoS was employed to provide the pertinent phase equilibrium data including accounting for CO_2 solids formation as a result of the significant temperature drop associated with the jet expansion process.

Typical fully expanded jet characteristics reported included its radius, temperature, density, fluid phase mass fraction and momentum flux.

The CFD simulations presented many of the expected subtle features of the jet behavior, including the shocks, the radial and axial decreases in the jet pressure and temperature followed by rapid recoveries at the Mach shock location and upon crossing the atmospheric boundary.

Using the generated CFD profiles, representative integrated average values of the jet characteristics were obtained. In order to demonstrate the impact of ignoring turbulence generation, the results were in turn compared against those from the existing integral models.

It was observed that in all the cases, within the range tested, although an increase in the upstream pressure results in an increase in the jet area, the expanded jet momentum upon reaching the surrounding ambient is relatively unchanged. Furthermore similar values for the jet thermodynamic properties such as density and internal energy were obtained as compared to those predicted from the CFD model, indicating negligible viscous dissipation during jet expansion.

However, the jet momentum flux was the parameter whose predicted magnitude was by far the most affected by the simulation technique employed. Here it was shown that ignoring turbulence generation during jet expansion results in as much as 50% overestimate of the jet momentum flux as compared to the CFD predictions. This overestimate was substantially reduced to a maximum of 15% when the mean kinetic energy loss associated with turbulence generation was incorporated in the developed integral model.

This finding has significant implications given that the jet momentum dictates the 'spread' of the subsequent dispersing cloud impacting many of its consequences including, where relevant its toxicity, flammability, explosion overpressure and ultimately the minimum safety distances to populated areas.

It should be noted that the jet expansion models presented in this study are based on the homogenous flow assumption. In the case of highly flashing flows, the finite evaporation or condensation rates along with relative acceleration between the fluid phases may result in thermodynamic and mechanical non-equilibrium. Also, as is the case with all mathematical models simulating real processes, where practical, validations against experimental data would be extremely useful. To this end, as part of the CO2QUEST project, we devoted significant effort in developing techniques for recording the jet expansion zone concentration, pressure and temperature immediately downstream of the release point. Unfortunately our attempts failed due to the extremely high momentum of the expanding jet which resulted in the damage and in some cases, the dislodging of the inline recording instrumentations.

Developing a computationally efficient non-equilibrium jet expansion model along with the construction of the robust instrumentation technology, including remote sensing for model validations are subjects of our ongoing work.

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ABBREVIATIONS

CCS, Carbon Capture and Sequestration; SST, Shear Stress Transport; PR-EoS, Peng-Robinson Equation of State; EPR-EoS, Extended Peng-Robinson Equation of State; IJEM, Integral Jet Expansion Model; IJEM-T, Integral Jet Expansion Model with Turbulence.

REFERENCES

(1) US Central Intelligence Agency. The world factbook [https://www.cia.gov/library/publications/the-world-factbook/fields/2117.html] (accessed June 5, 2016).

(2) Linnitt, M. Average 250 pipeline accidents each year, billions spent on property damage [http://www.desmog.ca/2013/04/05/average-250-pipeline-accidents-each-year-billions-spent-property-damage] (accessed June 1, 2016).

(3) Montiel, H.; Vilchez, J. A.; Amaldos, J.; Casal, J. Historical Analysis of Accidents in the Transportation of Natural Gas. *J. Hazard. Mater* **1996**, *51*, 77.

(4) Code of Federation Regulations, Title 49D, Part 195, Transportation of Hazardous Liquids by Pipeline; 2010.

(5) Global CCS Institute. *Strategic Analysis of the Global Status of Carbon Capture and Storage. Report 1: Status of Carbon Capture and Storage Projects Globally*; WorleyParsons: Canberra, 2009.

(6) International Energy Agency. *Scenarios & Strategies To 2050*. Paris 2010.

(7) Mahgerefteh, H.; Brown, S.; Denton, G. Modelling the Impact of Stream Impurities on Ductile Fractures in CO_2 Pipelines. *Chem. Eng. Sci.* **2012**, *74*, 200.

(8) Brown, S.; Martynov, S.; Mahgerefteh, H.; Proust, C. A Homogeneous Relaxation Flow Model for the Full Bore Rupture of Dense Phase CO_2 Pipelines. *Int. J. Greenh. Gas Control* **2013**, *17*, 349.

(9) Martynov, S.; Brown, S.; Mahgerefteh, H.; Sundara, V.; Chen, S.; Zhang, Y. Modelling Three-Phase Releases of Carbon Dioxide from High-Pressure Pipelines. *Process Saf. Environ. Prot.* **2014**, *92*, 36.

(10) Mahgerefteh, H.; Denton, G.; Rykov, Y. A Hybrid Multiphase Flow Model. *AIChE J.* **2008**, *54*, 2261.

(11) Witlox, H. W. M.; Harper, M.; Oke, A. Modelling of Discharge and Atmospheric Dispersion for Carbon Dioxide Releases. *J. Loss Prev. Process Ind.* **2009**, *22*, 795.

(12) Cleaver, R. P.; Edwards, P. D. Comparison of an Integral Model for Predicting the Dispersion of a Turbulent Jet in a Crossflow with Experimental Data. *J. Loss Prev. Process Ind.* **1990**, *3*, 91.

(13) Cleaver, R. P.; Cooper, M. G.; Halford, A. R. Further Development of a Model for Dense Gas Dispersion over Real Terrain. *J. Hazard. Mater.* **1995**, *40*, 85.

(14) Englund, S. M.; Bodurtha, F. T.; Britton, L. G.; Crowl, B. A.; Grossel, S.; High, W. G.; Kletz, T. A.; Ormsby, R. W.; Owens, J. E.; Schiappa, C. A.; Siwek, R.; White, R. E.; Winegardner, D.; Woodward, J. *Perry's Chemical Engineers' Handbook*, 7th ed.; Perry, R. H., Green, D. W., Maloney, J. O., Eds.; McGraw-Hill: New York, 2008.

(15) Witlox, H.; Harper, M.; Bowen, P.; Cleary, V. Flashing Liquid Jets and Two-Phase Droplet Dispersion. II. Comparison and Validation of Droplet Size and Rainout Formulations. *J. Hazard. Mater.* **2007**, *142*, 797.

(16) Calay, R. K.; Holdo, a E. Modelling the Dispersion of Flashing Jets Using CFD. *J. Hazard. Mater.* **2008**, *154*, 1198.

(17) Liu, X.; Godbole, A.; Lu, C.; Michal, G.; Venton, P. Source Strength and Dispersion of CO_2 Releases from High-Pressure Pipelines: CFD Model Using Real Gas Equation of State. *Appl. Energy* **2014**, *126*, 56.

(18) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.

(19) Transportation Research Board. Transmission Pipelines and Land Use: A Risk-Informed Approach. the National Academy of Sciences: Washington, D.C. 2004.

(20) Mikalauskas, K.; Urba, E.; Miškūnas, P.; Smirnov, D.; Burokas, A.; Miškinis, R. Realization of the Sublimation Temperature Point of Carbon Dioxide. *Lith. J. Phys.* **2013**, *53*, 127.

(21) Wareing, C. J.; Woolley, R. M.; Fairweather, M.; Falle, S. A. E. G. A Composite Equation of State for the Modeling of Sonic Carbon Dioxide Jets in Carbon Capture and Storage Scenarios. *AIChE J.* **2013**, *59*, 3928.

(22) Woolley, R. M.; Fairweather, M.; Wareing, C. J.; Falle, S. A. E. G.; Proust, C.; Hebrard, J.; Jamois, D. Experimental Measurement and Reynolds-Averaged Navier–Stokes Modelling of the near-Field Structure of Multi-Phase CO2 Jet Releases. *Int. J. Greenh. Gas Control* **2013**, *18*, 139.

(23) Brown, S.; Martynov, S.; Mahgerefteh, H.; Fairweather, M.; Woolley, R. M.; Wareing, C. J.; Falle, S. a E. G.; Rutters, H.; Niemi, A.; Zhang, Y. C.; Chen, S.; Besnebat, J.; Shah, N.;

Dowell, N. M.; Proust, C.; Farret, R.; Economou, I. G.; Tsangaris, D. M.; Boulougouris, G. C.; Wittenberghe, J. V. CO2QUEST: Techno-Economic Assessment of CO_2 Quality Effect on Its Storage and Transport. *Energy Procedia* **2014**, *63*, 2622.

(24) Woolley, R. M.; Fairweather, M.; Wareing, C. J.; Falle, S. A. E. G.; Mahgerefteh, H.; Martynov, S.; Brown, S.; Narasimhamurthy, V. D.; Storvik, I. E.; Sælen, L.; Skjold, L.; Economou, I. G.; Tsangaris, D. M.; Boulougouris, G. C.; Diamantonis, N.; Cusco, L.; Wardman, M.; Gant, S. E.; Wilday, J.; Zhang, Y. C.; Chen, S. Y.; Proust, C.; Hebrard, J.; Jamois, D. CO2PipeHaz: Quantitative Hazard Assessment for next Generation CO_2 Pipelines. In *Energy Procedia* **2014**, *63*, 2510.

(25) Woolley, R. M.; Fairweather, M.; Wareing, C. J.; Proust, C.; Hebrard, J.; Jamois, D.; Narasimhamurthy, V. D.; Storvik, I. E.; Skjold, T.; Falle, S. A. E. G.; Brown, S.; Mahgerefteh, H.; Martynov, S.; Gant, S. E.; Tsangaris, D. M.; Economou, I. G.; Boulougouris, G. C.; Diamantonis, N. I. An Integrated, Multi-Scale Modelling Approach for the Simulation of Multiphase Dispersion from Accidental CO_2 Pipeline Releases in Realistic Terrain. *Int. J. Greenh. Gas Control* **2014**, *27*, 221.

(26) Gant, S. E.; Narasimhamurthy, V. D.; Skjold, T.; Jamois, D.; Proust, C. Evaluation of Multi-Phase Atmospheric Dispersion Models for Application to Carbon Capture and Storage. *J. Loss Prev. Process Ind.* **2014**, *32*, 286.

(27) Hamzehloo, A.; Aleiferis, P. G. Large Eddy Simulation of Highly Turbulent under-Expanded Hydrogen and Methane Jets for Gaseous-Fuelled Internal Combustion Engines. *Int. J. Hydrogen Energy* **2014**, *39*, 21275.

(28) Irie, T.; Yasunobu, T.; Kashimura, H.; Setoguchi, T. Characteristics of the Mach Disk in the Underexpanded Jet in Which the Back Pressure Continuously Changes with Time. *J. Therm. Sci.* **2003**, *12*, 132.

(29) Dauptain, A.; Cuenot, B.; Giequel, L. Y. M. Large Eddy Simulation of a Stable Supersonic Jet Impinging on a Flat Plate. *AIAA J.* **2010**, *48*, 2325.

(30) Le Martelot, S.; Saurel, R.; Le Métayer, O. Steady One-Dimensional Nozzle Flow Solutions of Liquid–gas Mixtures. *J. Fluid Mech.* **2013**, *737*, 146.

(31) FlÅtten, T.; Morin, A.; Munkejord, S. T. On Solutions to Equilibrium Problems for Systems of Stiffened Gases. *SIAM J. Appl. Math.* **2011**, *71*, 41.

(32) Vandroux-Koenig, S.; Berthoud, G. Modelling of a Two Phase Momentum Jet close to the Breach, in the Containment Vessel of a Liquefied Gas. *J. Loss Prev. Process Ind.* **1997**, *10*, 17.

(33) Britter, R. E. Dispersion of Two-Phase Flashing Release - FLADIS Field Experiments; the Modelling of Pseudo-Source for Complex Releases. Report FM89/2 by CERC for EEC Commission DGXII (1994): Cambridge 1994.

(34) Britter, R. E. Dispersion of Two-Phase Flashing Releases - FLADIS Field Experiments; a Further Note on Modelling Flashing Releases. Report FM89/3 by CERC for EEC Commission DGXII: Cambridge 1995.

(35) Van den Bosch, C. J. H.; Duijim, N. J. *TNO Yellow Book - Methods for the Calculation of Physical Effects*, 3rd ed.; van den Bosch, C. J. H., Weterings, R. A. P. M., Eds.; Committee for the prevention of disasters, 1997.

(36) Pope, S. B. *Turbulent Flows*; Cambridge University Press: New York, 2000.

(37) George, W. K. Lectures in Turbulence for the 21st Century [http://www.uio.no/studier/emner/matnat/math/MEK4300/v13/undervisningsmateriale/tb_16january2013.pdf] (accessed May 8, 2015).

(38) Martynov, S.; Brown, S.; Mahgerefteh, H. An Extended Peng-Robinson Equation of State for Carbon Dioxide Solid-Vapor Equilibrium. *Greenh. Gases Sci. Technol.* **2013**, *3*, 136.

(39) Richards, P. J.; Norris, S. E. Appropriate Boundary Conditions for Computational Wind Engineering Models Revisited. *J. Wind Eng. Ind. Aerodyn.* **2011**, *99*, 257.

(40) Jacobson, M. Z. *Fundamentals of Atmospheric Modeling*, 2nd ed.; Cambridge University Press: New York, 2005.

(41) *ANSYS FLUENT User's Guide*; ANSYS, Inc.: Canosburg, 2013.

(42) Menter, F. R.; Kuntz, M.; Langtry, R. Ten Years of Industrial Experience with the SST Turbulence Model. In *Turbulence Heat and Mass Transfer 4*; Hanjalic, K., Nagano, Y., Tummers, M., Eds.; Begell House, Inc., 2003; pp 625.

(43) Sarkar, S.; Erlebacher, G.; Hussaini, M. Y.; Kreiss, H. O. The Analysis and Modelling of Dilatational Terms in Compressible Turbulence. *J. Fluid Mech.* **1991**, *227*, 473.

(44) Hébrard, J.; Jamois, D.; Proust, C.; Spruijt, M.; Hulsbosch-Dam, C. E. C.; Molag, M.; Messina, E. Medium Scale CO_2 Releases. *Energy Procedia* **2016**, *86*, 479.

(45) Moody, F. J. Maximum Flow Rate of a Single Component, Two-Phase Mixture. *J. Heat Transfer* **1965**, *87*, 134.

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