An Accurate and Efficient Look-up Table Equation of State for Two-Phase Compressible Flow Simulations of Carbon Dioxide

Yu Fang,*^{,†,‡} Marco De Lorenzo,[¶] Philippe Lafon,[¶] Sébastien Poncet,[‡] and Yann Bartosiewicz[†]

[†]Université Catholique de Louvain (UCL), 1348, Louvain-la-Neuve, Belgium

[‡]Département de génie mécanique, Université de Sherbrooke, 2500 Boulevard de l'Université, Sherbrooke, Quebec J1K 2R1, Canada [¶]IMSIA UMR EDF-CNRS-CEA-ENSTA, 91120, Palaiseau, France

S Supporting Information

ABSTRACT: This work presents an efficient and accurate method for the calculation of the properties of carbon dioxide. This is motivated by the massive employment of this fluid in the industrial domain, especially in the refrigeration industry through supersonic ejector cycles, and in the CO_2 capture and storage (CCS) industry. A tabulated equation of state (EoS) is developed in the density-internal energy space, based on the Span-Wagner EoS formulation which is the current international reference for computing CO_2 properties. The tabulated EoS is coupled to the Homogeneous Equilibrium Model to calculate properties of the liquid—vapor mixture. To assess the performance of the developed EoS, three configurations are simulated, namely a shock tube, a tube depressurization, and a



converging-diverging nozzle. Throughout the comparisons to other EoSs, such as the Peng-Robinson, the Stiffened Gas and the original Span-Wagner EoSs, the high efficiency of the tabulated equation of state is revealed.

1. INTRODUCTION

 CO_2 is considered a promising working fluid in the future of energy conversion, and in the refrigeration industry because of its low global warming potential (GWP = 1), and ozone depletion potential (ODP = 0). However, due to the thermodynamic properties of CO_2 , supercritical/transcritical operating conditions are usually encountered.^{1,2} For example, an ejector–expansion refrigeration system is shown in Figure 1 and the corresponding p-h diagram is shown in Figure 2. The ejector replaces the expansion valve to reduce the throttling



Figure 1. Schematic of a transcritical CO₂ refrigeration cycle with an ejector.



Figure 2. p-h diagram for the transcritical CO₂ refrigeration cycle with an ejector.

losses, and the compression effect produced by the ejector can also lower the compressor duty.^{3,4} The supercritical CO_2 coming from the gas cooler expands and flashes in the primary nozzle (from point 3 to point 4 in the p-h diagram). Then, the

 Received:
 February 1, 2018

 Revised:
 May 11, 2018

 Accepted:
 May 14, 2018

 Published:
 May 14, 2018

Industrial & Engineering Chemistry Research



Figure 3. Scheme to describe the A, B, and C iterative processes to find one, two, and three roots, respectively.

low-pressure jet from the primary nozzle can entrain the vapor from the evaporator where the refrigeration effect takes place (from point 9 to point 6). Then the two streams mix, and a compression effect is produced from point 6 to point 7 by exergy transfer between both streams. A part of the kinetic energy is recovered into pressure energy in the diffuser, and as a result, the efficiency of the refrigeration cycle is enhanced. In the liquid-vapor separator, a part of the liquid is used to feed the evaporator, while a part of the vapor is used to feed the compressor (from point 1 to 2 and from point 8 to 9). When the CO₂ flow is subjected to expansion followed by compression, complicated flow behavior can be encountered in the ejector, such as the formation of shock waves and twophase transition.⁵⁻⁸ Another industrial domain that involves O_2 is the O_2 capture and storage (CCS) industry which also reduces global warming. In the CCS industry, in order to moderate the cost to store and transport CO2, CO2 is usually transported in a dense liquid state or in the supercritical state at high pressures.^{9,10} The CO₂ leakage can cause a depressurization of the pipe associated with a large cooling effect. It can induce a rupture of the pipe and the propagation of cracks due to fluid-structure interactions.^{11,12} Hence, it is of prime importance to understand the behavior of CO₂ in pipe flows. Moreover, CO₂ can cause asphyxia from an accidental leak. People exposed to 10% concentration of CO₂ would quickly lost consciousness, and CO2 over 20% concentration becomes fatal.^{13,14} Over the past decade, numerical simulations were extensively used to predict realistic flow conditions either for the refrigeration industry with ejectors or the CCS industry in order to optimize the system design and operating conditions. It has been proven that the numerical results depend strongly on the thermodynamic properties of the CO₂ fluid in Computational Fluid Dynamics (CFD) simulations.^{15,16} Hence, the calculation of real and accurate thermodynamic properties of CO_2 is indispensable for a reliable numerical simulation. The Perfect-Gas (PG) EoS has been adopted by

Smolka et al.¹⁷ for the verification of their simulations. However, the PG EoS is not suitable to accurately compute the properties of supercritical states, liquid states, and twophase states. Morin et al.¹⁰ and Lund et al.¹⁸ applied the Stiffened-Gas (SG) EoS in the simulations of CO₂ pipe flows. However, the nonlinear behavior for liquid and supercritical states at the neighborhood of the critical point cannot be taken into account by the SG EoS becaue it is a linearized EoS around the reference thermodynamic state. Additionally, the choice of the reference states affects significantly the accuracy, considering a large range of flow states in the simulation.¹⁹ The Peng-Robinson EoS as a substitute of the Span-Wagner EoS or SAFT EoS has been used for CFD simulations of CO₂ pipe flows.² Later, the Span-Wagner (SW) EoS was considered by Hammer et al.¹¹ and Giljarhus et al.²¹ for the simulations of two-phase CO₂ pipe flows. However, due to the complexity of the SW EoS and flash calculations, for which iterative processes are used, the computational time could be considerably long. In general, three types of iterative processes can be encountered in the simulations, the objectives of which are to find one, two, or three unknown variables as described in Figure 3 charts A, B, and C, respectively. For example, in order to determine a phase-equilibrium state, the saturated temperature and the vapor quality should be computed by giving the density and the internal energy. In this case, algorithm C is used. Similar to the SW EoS, Yazdani et al.²² and Colarossi et al.²³ used Refprop²⁴ for property calculations, and it provided fairly good numerical results for two-phase CO₂ ejectors, but computational time was prohibitively high as well.

Span-Wagner (SW) EoS is known as an international reference EoS for CO_2 covering, a wide range of temperature and pressure, from the triple-point temperature to 1100 K and the pressure up to 800 MPa.²⁵ SW EoS was obtained by fitting hundreds of parameters with extensive experimental data and is able to provide accurate values near the critical point (in the critical region). This EoS is very accurate but extremely costly

Article

from a computational point of view. It has been already implemented in Refprop²⁴ and Coolprop²⁶ to predict CO_2 properties.

To realize massive CFD simulations (i.e., 3D unsteady largeeddy simulation), both accuracy and computational efficiency requirements should be fulfilled. The look-up table method is a good candidate to satisfy these two requirements. It has been investigated for water-steam fast transient simulations in nuclear thermodynamics^{27,28} and cavitating flows.²⁹ The tabulated thermodynamic properties are precomputed ahead of time and stored as a database in the memory. Then, at each time step during the simulation, the property values are calculated by an interpolation algorithm from the database. This procedure is quasi-instantaneous, even faster than using an analytical EoS. A look-up-table method in the (v,e) (the specific volume and the specific internal energy) space has been recently proposed for water,²⁷ and this work extends this approach for CO₂. Similar work has also been done based on the Perturbed Chain-SAFT (PC-SAFT) for simulations of depressurization of the CO2-rich mixtures.^{30,31} Besides, Ameli et al.,³² and Giacomelli et al.,³³ proposed a Refprop-based lookup table method for two-phase CO₂ ejector simulations. However, a commercial database does not give the flexibility of a full in-house approach to optimize both accuracy and CPU time, as well as using more advanced two-phase models (for example, the Homogeneous Relaxation Model, Delayed Equilibrium Model).³

Hence, in this paper, an in-house tabulated EoS approach based on SW EoS is developed to ensure, on one side, a high accuracy, and on the other side, a high computing efficiency (5.3). The density ρ (or specific volume $\nu = 1/\rho$), and the specific internal energy e are chosen as two appropriate, and independent variables because they are more suitable for a hyperbolic equation system in its conservative form. Consequently, the pressure, temperature, and speed of sound are computed from a given pair of variables (ρ, e) with the tabulated EoS. A bilinear algorithm is employed for the interpolation process based on the tabulated values. Additionally, the bilinear interpolation method shows reasonable errors compared to exact values computed directly by the original SW EoS. The look-up table interpolation technique has been coupled to an Homogeneous Equilibrium Model (HEM) implemented into the CLAWPACK^{36,37} solver to provide 1D and 2D simulations. The adopted Riemann solver is the Harten-Lax-van Leer-Contact (HLLC),^{36–38} which can be readily coupled to any EoS. To the best of the authors' knowledge, a Span-Wagner-based look-up table method for pure CO₂ has never been published in the literature.

This paper is organized as follows. In section 2, the hyperbolic equations system, and the HEM are briefly described. Section 3 explains the construction of the tabulated domain in the e-v space, the mapping of the e-v space, and the bilinear interpolation technique. The difference between the interpolated values and the exact values from the original Span–Wagner EoS is also illustrated at the end of this section. In section 4, the HLLC Riemann solver used to solve the hyperbolic system in its conservative form is described, as well as the coupling procedure with the tabulated EoS. In section 5, different benchmarks are presented in order to assess the tabulated EoS against other EoSs such as the PR EoS, the SG EoS and the original SW EoS. Finally, a 2D supersonic CO₂ nozzle is investigated to assess the capacity of the tabulated EoS to deal with compressible two-phase flow simulations.

2. HYPERBOLIC SYSTEM-HOMOGENEOUS EQUILIBRIUM MODEL

Several models for two-phase flows have been developed in the literature. In the scope of two-phase compressible flows, the most complete model is the seven-equation model proposed by Baer and Nunziato,³⁹ in which the two phases are assumed in full nonequilibrium in terms of temperature, pressure, and velocity. A six-equation model was provided by Pelanti and Shyue,⁴⁰ and Saurel et al.,⁴¹ which considers that the twophases are in thermodynamic nonequilibrium. Regarding twophase models for supersonic ejector flows, Mazzelli et al.⁴² modeled condensation by means of the wet steam model.⁴³ The Homogeneous Relaxation Model (HRM)^{34,44} was applied by Colarossi et al.²³ The thermodynamic nonequilibrium between the two phases is accounted by a relaxation time. The most considered two-phase model for CO₂ supersonic ejector simulation is the HEM used by Lucas et al.,⁴⁵ Palacz et al.^{46,47} and Smolka et al.,¹⁷ in which the temperature, pressure, and velocity of the two phases are supposed to be in full equilibrium. Palacz et al.⁴⁷ compared the accuracy between the HEM and the HRM for two-phase CO₂ ejector simulation and stated that the differences between the HEM and HRM depended strongly on operating conditions. For the operating regimes close to the CO₂ critical point, the HEM provided more accurate results than the HRM.

With the aim of presenting the versatility, and the advantages of the tabulated EoS for the two-phase CO_2 simulation, the HEM is chosen primarily for simplicity. However, any of the existing more advanced models could be coupled to this proposed EoS as well, as shown in ref 27. Considering the HEM, it is defined by a set of three partial differential equations consisting of the conservation of mass (eq 1), the conservation of momentum (eq 2), and the conservation of total energy (eq 3) for the two-phase mixture. In one dimension the set of equations reads:

$$\partial_t \rho + \partial_x (\rho u) = 0 \tag{1}$$

$$\partial_t(\rho u) + \partial_x(\rho u^2 + p) = 0 \tag{2}$$

$$\partial_t(\rho E) + \partial_x[(\rho E + p)u] = 0 \tag{3}$$

The system is written under its conservation form and the conservative variables are ρ the density, ρu the momentum, and ρE the total energy of the mixture. u and E denote the velocity of the mixture and its specific total energy, respectively, $E = e + u^2/2$, where e is the specific internal energy. A compact 1D formulation is

$$\partial_t U + \partial_x F(U) = 0 \tag{4}$$

where U is the vector form of the conservative variables and the F represents the flux vector, expressed as

$$U = \begin{bmatrix} \rho \\ \rho u \\ \rho E \end{bmatrix}, \quad F = \begin{bmatrix} \rho u \\ \rho u^2 + p \\ u(E+p) \end{bmatrix}$$
(5)

This nonlinear hyperbolic conservative equations system governs the dynamics of the inviscid, and adiabatic compressible two-phase flow without body forces. It has formally the same structure as the single-phase Euler system. A similar numerical method can be then applied for the HEM system, as discussed in section 4. The full thermodynamic and mechanical equilibrium assumed in the HEM leads to the following constraints:

$$p_{1} = p_{v} = p_{sat},$$

$$T_{1} = T_{v} = T_{sat},$$

$$u_{1} = u_{v} = u,$$

$$g_{1} = g_{v} = g$$
(6)

where the subscripts 1 and v denote the liquid and the vapor phases, respectively. The term *g* represents the specific Gibbs free energy, g = h - Ts, where *h* is the specific enthalpy, *T* is the temperature, and *s* is the specific entropy. For two-phase states, the liquid and the vapor are saturated, with the specific internal energy and the specific volume of the mixture being:

$$e = xe_{v} + (1 - x)e_{l},$$

$$v = xv_{v} + (1 - x)v_{l}$$
(7)

where $e_{\rm b} v_{\rm b} e_{\rm v}$, and $v_{\rm v}$ are the quantities at saturation, $v = 1/\rho$ and x is the vapor quality, expressed as in the HEM frame:

$$x = \frac{h - h_l}{h_g - h_l} \tag{8}$$

where the specific enthalpy h is written as h = e + pv.

Analyzing the eigenvalues of the Jacobian of the vector F reported in eq 4, one can determine the speed of sound of the model.²⁷ The proposed formulation for the speed of sound in the HEM is detailed in Appendix A. The evaluation of the two-phase speed of sound respect to the void fraction is shown in Figure 4 using the relations of Wood,⁴⁸ Nakagawa et al.,⁶



Figure 4. Two-phase speed of sound at p = 5.03 MPa computed by the HEM. Comparisons with the relation of Wood,⁴⁸ the relation of Nakagawa et al.⁶ and the relation of Ameur et al.⁴⁹

Ameur et al.⁴⁹ and the proposed relation for the HEM. Figure 4 shows that the two-phase speed of sound of the HEM has two discontinuities for $\alpha_v = 1$ and $\alpha_v = 0$, which implies discontinuities through the saturation curve. These discontinuities are model-dependent, as discussed by Flätten and Lund,⁴⁴ and Nakagawa et al.⁵⁰

In the system composed of eqs 1, 2, 3, there are four unknowns but only three equations. In order to close the system, an EoS is required to compute the pressure $p(e, \rho)$ from the density and the specific internal energy. In the next section, the tabulated EoS procedure to determine the thermodynamic properties is illustrated.

3. EQUATION OF STATE AND LOOK-UP TABLE METHOD FOR CO₂

The density ρ and the specific internal energy e can be computed directly from eq 1 and eq 3. Thus, the most natural way to determine the thermodynamic properties is to use a pair of variables, (ρ, e) , such as for the pressure, $p = p(\rho, e)$. The latter is called an incomplete EoS. Complete EoSs are usually described in terms of Helmholtz free energy, and the independent variables are the temperature and the density, such as for the Span-Wagner EoS. Constructing an incomplete EoS with SW EoS, requires inversion procedures. For example, for the pressure calculation when ρ and e are initially known, the temperature should be computed iteratively by a one rootfinding method, then the pressure is computed by SW EoS with (ρ, T) . The iterative process is shown in Figure 3. Consequently, direct use of SW EoS requires a high computational cost and is not always stable. Initial guesses are important for an iterative process. They determine the stability and the speed of convergence. Hence, the use of the iterative process in CFD simulations is not suitable due to the possibility of bad initial guesses according to the method. In a numerical simulation, the EoS is needed at each time step for each mesh-node, thus a fast EoS can significantly improve efficiency of the entire simulation. The look-up table method can achieve high efficiency. The inversion algorithms are used at the mesh construction stage in the preprocessing, and the properties at the mesh nodes are stored in the memory. During the simulation, the fluid properties are calculated by interpolations. A similar method has been developed for the fast calculation of water-steam properties.^{27,28,51}

The look-up table method can not only be extremely efficient but can also reach high accuracy. It has been used in several CFD codes^{52,53} for water, but iterative algorithms were still involved depending on the construction of the EoS. For the proposed tabulated EoS, the whole region is tabulated except in the tiny region between two subdomains (the detailed explanations are presented in section 3.2). Another advantage of the tabulation strategy is that once the variables (ρ , e) are known, the phase location in the $e-\nu$ space is determined; therefore, the evolution of the phase state during numerical simulations can be monitored and the location of the onset of the phase change can be determined.

3.1. Span-Wagner EoS. Span-Wagner EoS²⁵ is considered as the most reliable EoS for CO₂. It is an EoS based on hundreds of parameters that are fitted by extensive experimental data in terms of pressure, heat capacity, speed of sound, and other thermodynamic properties. The formulation stems from the specific Helmholtz free energy A, in dimensionless form $\phi = A/RT$, respect to the reduced temperature, $\tau = T_c/T$, and the reduced density, $\delta = \rho/\rho_c$; ρ_c and T_c are the critical density and temperature, respectively. The formulation reads:

$$\phi(\delta, \tau) = \phi^{0}(\delta, \tau) + \phi^{r}(\delta, \tau)$$
⁽⁹⁾



Figure 5. Flowchart for the look-up table method. Detailed steps are described in section 3.2.



Figure 6. e-v diagram in the physical domain with pressure from 0.5 MPa to 50 MPa and temperature from 216.5 K to approximate 800 K. The dashed line on the left denotes the isobaric line of 50 MPa, whereas the right dashed line denotes the isobaric line of 0.5 MPa. The saturation curve is divided by the critical point, and the liquid saturation curve is presented by the blue line, whereas the vapor saturation line is presented by the purple and yellow lines. The red line on the top represents the internal energy corresponding approximately 800 K. Three iso-energy lines divide the whole domain into some subdomains, namely LL, LH, HT, and R for single phases, and TPH, TPM, and TPL for two phases.

where ϕ consists of two parts, the ideal part ϕ^0 and the residual part ϕ^r . The other properties can be derived from the combination of the first and second derivatives of the Helmholtz energy, such as the pressure and the speed of sound:

$$p(\delta, \tau) = \rho RT (1 + \delta \phi_{\delta}^{1})$$
⁽¹⁰⁾

$$c^{2}(\delta, \tau) = RT \left(1 + 2\delta\phi_{\delta}^{r} + \delta^{2}\phi_{\delta\delta}^{r} - \frac{(1 + \delta\phi_{\delta}^{r} - \delta\tau\phi_{\delta\tau}^{r})}{\tau^{2}(\phi_{\tau\tau}^{0} + \phi_{\tau\tau}^{r})} \right)$$
(11)

where the subscript δ and τ represent the derivatives respectively to δ and τ . For this work, the SW EoS has been primarily implemented in an *in-house* FORTRAN code and used later for the tabulation.

3.2. The Look-up Table Method. A flowchart, shown in Figure 5 is depicted to describe the procedure of the look-up table method. First, the e-v space presented in Figure 6 is meshed. Then, pressure, temperature, and speed of sound are

computed by the original SW EoS with iterative algorithms at each node with (e, v) as the coordinates. As the interpolation is performed in the transformed space, thus the e-v space is then transformed to the X-Y space, illustrated in Figure 9 and the interpolation coefficients are computed for each property. Finally, the pressure, the temperature and the speed of sound can be obtained by the bilinear interpolation of the node values stored in the memory. As mentioned above, the tabulated method is not used in the whole domain, because the accuracy of the interpolation is not good enough at the boundary between the LH domain and the HT domain in Figure 6. Therefore, the original SW EoS is used in this tiny region coupled to the Newton-Raphson method. The tabulated values are considered as initial guesses to ensure the speed and the stability of the convergence. Normally, the number of the iterations is less than six.

Figure 6 illustrates the e-v diagram, called also the physical domain in the following. The e-v diagram is not a frequent representation of the thermodynamic properties compared to



Figure 7. Isobaric curves in the $e-\nu$ diagram.







Figure 9. Mapped physical space and X-Y space. The numbering of vertices for one cell starts from the left bottom corner and is counted in the clockwise direction.²⁷

(p-T) or (T-s) diagrams, in which the saturation curve has the form of the usual tome. The blue curves surround the liquid region while the purple curves surround the supercritical region and the vapor region is wrapped by the red and yellow curves. The region under the saturation line represents the two-phase region. Figure 7 and Figure 8 show the isobaric lines and the isothermal lines provided by the tabulated EoS. The maximum pressure is fixed at 50 MPa as the left boundary. The minimum pressure is fixed to the triple point pressure, p = 0.5 MPa as the right boundary, whereas the maximum internal energy corresponding to approximate 500 K fixes the top boundary. The bottom boundary is the internal energy of the triple point of liquid. In the region with pressures smaller than 0.5 MPa, the PG EoS is applied. The ranges in terms of pressure and

temperature are sufficiently large to cover most of industrial applications involving CO_2 . Moreover, the pure solid, solid–vapor, liquid–solid, and liquid–vapor–solid states are not included in the proposed approach.

3.2.1. Grid Construction in the e-v Space. The left-low (LL), left-high (LH), right (R), and two-phase (TP) domains are meshed with equidistant pattern of nodes, whereas the high-temperature (HT) domain uses a logarithmic distribution of nodes. The two-phase region is divided to three subdomains: two-phase high (TPH), two-phase middle (TPM) and two-phase low (TPL) subdomains by the iso-line of the critical internal energy and the triple-point internal energy of vapor (see Figure 6). Each domain is meshed with 10 000 nodes. In

Article



Figure 10. Relative errors for the pressure in the e-v space.

total, 70 000 nodes are necessary to compute pressure, temperature, and speed of sound in the physical domain.

3.2.2. Transformation from Irregular Physical Space to X– Y Cartesian Space. To improve the accuracy of the bilinear interpolation, the irregular mesh (parallelogram) in the e-vspace is transformed to a X - Y Cartesian space with square cells, as shown in Figure 9. The size of the X-Y space is chosen initially, here each cell in the X-Y space is fixed to unity. The numbers of cells in the e-v space and in the X-Y space are imposed to be equal. A transformation function is defined to rescale the irregular mesh to the regular square-form mesh:

$$\Phi \colon \mathbb{R}^2 \to \mathbb{R}^2 \quad \text{such that:} \quad \forall \ (v, e) \in \mathcal{D} \Rightarrow (X, Y) \in \mathcal{D}'$$
(12)

where \mathcal{D} and \mathcal{D}' denote the physical, and transformed spaces, respectively. The internal energy is meshed equidistantly in both spaces, thus *e* is linearly scaled to *Y* (eq 13). On the contrary, the scaling coefficients for *v* are energy-dependent, because in the e-v space, the boundary values for *v* are different and correspond to each level of the internal energy (eq 14). Therefore, the transformation function for the mesh is written as

$$e_i = A + BY_i \tag{13}$$

$$v_{i,j} = C(e_i) + D(e_i)X_{i,j}$$
(14)

The coefficients *A* and *B* are constant values and *C* and *D* are variables depending on *e*, which are determined by the spline construction of the domain boundary. The subscripts *i* and *j* represent the node number in the *e* (*Y*) and *v* (*X*) directions, respectively. As a result, all the nodes in the *e*–*v* space matche the nodes in the *X*–*Y* space. Then the bilinear interpolation is performed in the *X*–*Y* space. Before starting the interpolation procedure, the location of the phase state should be determined in the *X*–*Y* space. As same manner as before, a pair (e_0 , v_0) is determined in the *X*–*Y* space, (X_0 , Y_0), by inverting eq 13 and eq 14. Once (X_0 , Y_0) are obtained, the coordinates (*i*, *j*) of the vertices are obtained by

$$i = int\left(\frac{Y_0 - Y_{\min}}{\Delta Y}\right), \ j = int\left(\frac{X_0 - X_{\min}}{\Delta X}\right)$$
(15)

where (i, j) indicate the numbering of the cell, to which (X_0, Y_0) belong.

3.2.3. Bilinear interpolation. The interpolation coefficients should be computed to determine the bilinear interpolation

function in each cell (i, j).^{54,55} For example, the function for the pressure in each cell is computed as

$$\tilde{p}_{i,j} = \gamma_{i,j}^1 + \gamma_{i,j}^2 X_{i,j} + \gamma_{i,j}^3 Y_i + \gamma_{i,j}^4 X_{i,j} Y_i$$
(16)

where $\tilde{p}_{i,j}$ is the value from the bilinear interpolation. The coefficients $\gamma_{i,j}^k$ correspond to the *k* vertices in the (i, j) cell. They are obtained by solving the system constructed by the pressure at the four vertices of the cell (i, j) in the *X*-*Y* space whose values in the *e*- ν space can be expressed as

The pressure at the four vertices, p_1 , p_2 , p_3 , p_4 are obtained by the original SW EoS at the grid construction stage. The explicit expressions of each coefficient read as

$$\gamma^{1} = p_{1}, \quad \gamma^{2} = -p_{1} + p_{4}, \quad \gamma^{3} = -p_{1} + p_{2},$$

 $\gamma^{4} = p_{1} - p_{2} + p_{3} - p_{4}$
(18)

Once γ_i is determined, one can obtain directly the pressure after determining the position of the couple (e_0, ν_0) in the transformed space (X_0, Y_0) by

$$p(e_0, v_0) = \tilde{p}(X_0, Y_0) = \gamma_1 + \gamma_2 X_0 + \gamma_3 Y_0 + \gamma_4 X_0 Y_0$$
(19)

Other properties such as the speed of sound and the heat capacity can be obtained in the same manner as described above.

Before the numerical simulation, it takes around 10 s to construct the grid and compute the interpolation coefficients. During the simulation, the thermodynamic properties are obtained directly by the bilinear interpolation (similar formulation as eq 19). Contrary to the splined-based interpolation proposed by Kunick et al.²⁸ and the bicubic interpolation applied by De Lorenzo et al.²⁷ for the water properties, the continuity of the derivatives of the tabulated properties through the cell boundary is not ensured. But a large number of nodes are computed in each subdomain to make the tabulated properties sufficiently smooth in the whole e-v space. No numerical issue has been encountered caused by the discontinuity of the property in the numerical cases below. Moreover, regarding the derivatives of speed of sound and

Article





temperature, they are rarely required by numerical simulations. Even if the derivatives of pressure are needed, they can be evaluated analytically by the original SW EoS. In addition, the thermodynamic consistency is satisfied naturally through the construction of pressure, entropy, and internal energy by the SW EoS.⁵⁶ Considering the simple construction, the bilinear interpolation is less time-consuming and shows a quite good accuracy for numerical simulations. Figure 10 displays the relative errors between the original SW EoS and the bilinear interpolation values in terms of pressure, whereas Figure 11 displays the absolute errors in terms of temperature. Twentyfive test-points are calculated inside each cell in the single-phase region and 250 000 points in the whole two-phase region to assess the accuracy of the bilinear interpolation, which make 2 million checkpoints in total. The map of the relative errors of the speed of sound is not shown here, but the maximum relative errors are presented in Table 1 as well as for the

Table 1. Maximum Relative Errors for the Pressure and the Speed of Sound and the Maximum Absolute Errors for the Temperature

domain	max error for p [%]	max error for $T[K]$	max error for c [%]
LL	0.16	0.007	1.2
LH	0.05	0.04	0.2
HT	0.23	0.05	0.08
R	0.20	0.06	0.01
TP	0.07	0.03	

pressure and the temperature. It is observed that the properties are predicted fairly well in each subdomain. The maximum error for the speed of sound is around 1.2%, this max being located in the neighborhood of the critical point. The critical region is often an issue for evaluating the thermodynamic properties, because some properties such as the speed of sound and the heat capacity have a singularity at the critical point and therefore exhibit great nonlinear behavior near the critical point. Even through the SW EoS is considered as the most accurate EoS in the critical region, it still has more than 1% uncertainty in terms of speed of sound near the critical point. Moreover, it is verified that the nearest nodes to the critical point in the LL, LH, and TP subdomains have a pressure difference between 92 Pa and 1600 Pa and a temperature difference between 0.001 K to 0.09 K. These nodes define the properties in the nearest region to the critical point.

In summary, the proposed tabulated EoS shows a quite good accuracy in the whole range from 0.5 MPa to 50 MPa for the

pressure and from 217 K to 500 K for the temperature. It shows also the capacity to accurately and stably evaluate the properties in the critical region.

4. HLLC-TYPE RIEMANN SOLVER

The proposed tabulated EoS is implemented in the opensource software CLAWPACK.³⁶ It solves hyperbolic systems in 1D and 2D by using the wave propagation method.^{36,37} This method is classified as a Godunov-type finite volume scheme,⁵⁷ and a HLLC-type Riemann solver is implemented to solve the Riemann problem at each interface of the cells.^{38,58} In the subsequent sections, the main ideas of the numerical method are described in 1D and 2D, respectively. Besides, the HLLCtype solver is presented at the end of this section.

4.1. One-Dimensional Wave-Propagation Method. The hyperbolic system composed of eqs 1, 2 and 3 can be discretized on a uniform one-dimensional grid with a constant spatial step Δx . The time-integration is achieved using the Euler explicit scheme with the time step Δt . Q_i^n denotes the approximate value of the variable U (eq 4) averaged over the *i*th



Figure 12. 1D finite volume method for updating *Q* in the x-t space.

cell at time t_n (Figure 12). The approximate solution Q in cell i is updated at each time step as

$$\mathbf{Q}_{i}^{n+1} = \mathbf{Q}_{i}^{n} - \frac{\Delta t}{\Delta x} (\mathcal{A}^{+} \Delta \mathbf{Q}_{i-1/2} + \mathcal{A}^{-} \Delta \mathbf{Q}_{i+1/2}) + \frac{\Delta t}{\Delta x} (\tilde{\mathbf{F}}_{i-1/2}^{2nd} - \tilde{\mathbf{F}}_{i+1/2}^{2nd})$$
(20)

In Figure 12, the fluxes at the interfaces of the cell *i*, $F_{i-1/2}^n$ and $F_{i+1/2}^n$, are decomposed into fluctuation terms and correction terms. $\mathcal{R}^{\pm}\Delta Q_{i\pm 1/2}$ is called fluctuations at the interface $i \pm \frac{1}{2}$, where the superscripts + and – of \mathcal{R} indicate the right-going

and left-going fluctuations, respectively. $\tilde{F}_{i\pm 1/2}^{2nd}$ represent the correction terms for the flux to achieve a second-order accuracy. The fluctuation at the interface can be obtained as³⁷

$$\mathcal{A}^{+} \Delta \mathbf{Q}_{i-1/2} = \sum_{m=1}^{M} s_{i-1/2}^{m+} \mathcal{W}_{i-1/2}^{m},$$
$$\mathcal{A}^{-} \Delta \mathbf{Q}_{i+1/2} = \sum_{m=1}^{M} s_{i+1/2}^{m-} \mathcal{W}_{i+1/2}^{m}$$
(21)

where s^{\pm} is the wave right- and left-propagating speed and W is the variation of the variables across the propagating waves. M is the number of waves in the system (eqs 1, 2, and 3). Here, the one-dimensional Euler system is composed of three waves



Figure 13. Three waves define four piecewise constant states for the Riemann problem.

(see Figure 13). The second-order accuracy is obtained by adding the correction fluxes:

$$\tilde{\mathbf{F}}_{i+1/2}^{2nd} = \frac{1}{2} \sum_{m=1}^{M} |s_{i+1/2}^{m}| \left(1 - \frac{\Delta t}{\Delta x} |s_{i+1/2}^{m}|\right) \tilde{\mathcal{W}}_{i+1/2}^{m,2nd},$$

$$\tilde{\mathbf{F}}_{i-1/2}^{2nd} = \frac{1}{2} \sum_{m=1}^{M} |s_{i-1/2}^{m}| \left(1 - \frac{\Delta t}{\Delta x} |s_{i-1/2}^{m}|\right) \tilde{\mathcal{W}}_{i-1/2}^{m,2nd},$$
(22)

where $\tilde{W}_{i\pm1/2}^{m,2nd}$ denotes a modified wave strength based on a limiter function.³⁷ Hereafter a Riemann solver can give at each interface the wave strength W, and the associated wave propagation speed, *s*, is obtained by the formulation of Davis.⁵⁹

4.2. Two-Dimensional Wave-Propagation Method. In two dimensions, the formulation is similar. The updating of the numerical solution $Q_{i,j}$ from t_n to t_{n+1} is expressed as

$$\mathbf{Q}_{i,j}^{n+1} = \mathbf{Q}_{i,j}^{n} - \frac{\Delta t}{\Delta x} (\mathcal{A}^{+} \Delta \mathbf{Q}_{i-1/2,j} + \mathcal{A}^{-} \Delta \mathbf{Q}_{i+1/2,j}) - \frac{\Delta t}{\Delta y} (\mathcal{B}^{+} \Delta \mathbf{Q}_{i,j-1/2} + \mathcal{B}^{-} \Delta \mathbf{Q}_{i,j+1/2}) + \frac{\Delta t}{\Delta x} (\tilde{\mathbf{F}}_{i-1/2,j}^{h} - \tilde{\mathbf{F}}_{i+1/2,j}^{h}) + \frac{\Delta t}{\Delta y} (\tilde{\mathbf{G}}_{i,j-1/2}^{h} - \tilde{\mathbf{G}}_{i,j+1/2}^{h})$$
(23)

where $\mathcal{A}^+\Delta \mathbf{Q}$ and $\mathcal{B}^+\Delta \mathbf{Q}$ are the fluctuations at the interface in the *x* and *y* directions. The correction fluxes $\tilde{\mathbf{F}}^h$ and $\tilde{\mathbf{G}}^h$ consist of second-order corrections and contributions of the transverse fluctuations.⁴⁰ Here, a dimensional splitting strategy is considered: the 1D Riemann solver is applied separately for x and y directions at each time step.³⁷ This strategy may introduce a splitting error. LeVeque³⁷ mentioned that the splitting error is often of the same order as the errors due to the numerical method. Hence, the dimensional splitting approach could give an inexpensive technique for two- or three-dimensional simulations.

Furthermore, the formulation of eq 23 which relies on a Cartesian grid is extended to quadrilateral grids (curvilinear grids) through a conform transformation for more complex computational domains.^{37,60}

4.3. HLLC-Type Riemann Solver. The HLLC-type solver of Toro³⁸ is implemented in the CLAWPACK solver to solve the local Riemann problem at the cell interface to provide the wave strength \mathcal{W}^m . This type of solver has some attractive features: first, it is able to capture clean and sharp discontinuities such as shock waves and contact surfaces. Second, it is robust and efficient for nonideal gases compared to the exact Riemann solver.

Here, in one dimension, the configuration of three waves separating four states, \mathbf{Q}_L , \mathbf{Q}_L^* , \mathbf{Q}_R^* , and \mathbf{Q}_R are assumed, as depicted in Figure 13. The left and right acoustic waves are called nonlinear waves and they can be either shocks or rarefactions, propagating with speed $s^1 = S_1$ and $s^3 = S_r$. The middle wave propagates at $s^2 = S_*$. Following Davis,⁵⁹ the wave speeds are estimated as

$$S_{l} = \min(u_{l} - c_{l}, u_{r} - c_{r}), S_{r} = \max(u_{l} + c_{l}, u_{r} + c_{r})$$
(24)

To calculate *S*_{*}, Toro⁵⁸ proposed:

$$S_{*} = \frac{p_{\rm r} - p_{\rm l} + \rho_{\rm l} u_{\rm l} (S_{\rm l} - u_{\rm l}) - \rho_{\rm r} u_{\rm r} (S_{\rm r} - u_{\rm r})}{\rho_{\rm l} (S_{\rm l} - u_{\rm l}) - \rho_{\rm r} (S_{\rm r} - u_{\rm r})}$$
(25)

The left and right-state sound speeds $c_{\nu} c_r$ and the pressure $p_{\nu} p_r$ correspond to the local thermodynamic states. They are obtained by the tabulated EoS. Furthermore, the middle states are obtained as⁵⁸

$$\mathbf{Q}_{K}^{*} = \rho_{K} \left(\frac{S_{K} - u_{K}}{S_{K} - S_{*}} \right) \\ \begin{bmatrix} 1 \\ S_{*} \\ \frac{E_{K}}{\rho_{K}} + (S_{*} - u_{K}) \left[S_{*} + \frac{p_{K}}{\rho_{K}(S_{K} - u_{K})} \right] \end{bmatrix}$$
(26)

where K = l, r then the wave strengths are computed as

$$\mathcal{W}^{1} = \mathbf{Q}_{L}^{*} - \mathbf{Q}_{L'} \qquad \mathcal{W}^{2} = \mathbf{Q}_{R}^{*} - \mathbf{Q}_{L'}^{*}$$
$$\mathcal{W}^{3} = \mathbf{Q}_{R} - \mathbf{Q}_{L}^{*} \qquad (27)$$

where \mathbf{Q}_{L} takes the average value of the conservative variables in cell *i* – 1, \mathbf{Q}_{i-1} (Figure 13), while \mathbf{Q}_{R} is equal to that of cell *i*, \mathbf{Q}_{i} (Figure 13). Finally, \mathcal{W} and *s* are determined to compute the fluctuations at the interface through eq 21.

In the following section, several numerical simulations are carried out for single phase and two-phase CO_2 flows to assess the performance of the tabulated EoS in numerical simulations.



Figure 14. Schematic of the shock tube problem. The left side is filled with the high pressure CO_2 while the right side is filled with the low pressure CO_2 .



Figure 15. Pressure, density, velocity, and temperature profiles at t = 0.08 s for the shock tube problem. Comparison with the numerical results of Giljarhus et al.²¹ Numerical data from Giljarhus et al.²¹

5. NUMERICAL EXPERIMENTS

A series of benchmark verifications is presented in this section to highlight the capacity of the tabulated EoS to deal with twophase CO_2 simulations. The experimental database of the single-phase and two-phase CO_2 flows is far from abundant in the literature. Consequently, the numerical results are utilized to validate the proposed approach, as shown in sections 5.1 and 5.2 for the shock tube case and the depressurization case. In section 5.3, the results are compared to the Peng–Robinson, the Stiffened-Gas, and the Span-Wagner EoS. A two-dimensional converging–diverging nozzle is then investigated and compared to the available experimental measurements in section 5.4.

5.1. Shock tube. In this section, a classic shock tube problem is considered to assess the accuracy of the tabulated EoS for the CO_2 vapor. As shown in Figure 14, a 100-m tube is filled with CO₂ at two different vapor states separated by a membrane at the middle of the tube. Initially, the left state is at $p_{\rm L}$ = 3 MPa, $T_{\rm L}$ = 300 K and $\rho_{\rm L}$ = 63.376 kg·m^{-3} at rest, while the right state is at $p_{\rm R}$ = 1 MPa, $T_{\rm R}$ = 300 K and $\rho_{\rm R}$ = 18.579 kg· m^{-3} at rest. At t = 0, the membrane is removed and the high pressure CO₂ interacts with the low pressure CO₂. The leftpropagating expansion waves form while a contact surface and a shock wave are generated and propagate toward the right. The 1D tube is meshed with 1000 grid points. Figure 15 illustrates the pressure, density, velocity, and temperature distributions along the tube at t = 0.08 s. The numerical results agree perfectly with the results of Giljarhus et al.²¹ in which 1000 points along a 100 m tube were simulated. MUSTA (MUlti-STage Approach) was used to solve the Euler equations by using the original SW EoS associated with a centered method for the interface flux construction.^{61,62} This approach is an

alternative method to avoid using a Riemann solver. It could provide comparable results to an upwind method. However, little differences at the discontinuities especially at the contact surface could be obtained, which is also observed in Figure 15. But regarding the remainder of parts except the discontinuities, this validation case presents that the tabulated EoS can reach the same accuracy as the original SW EoS for the CO_2 vapor simulation.

5.2. Depressurization. The CO_2 fluid transported in the pipeline or stored in the tank remains often in the dense phase (pressure higher than the critical pressure). Damage of the container wall or the rupture of the pipeline can cause the pressure to drop rapidly, at which the CO_2 fluid is subjected to a violent phase transition, known as "flashing". A large amount of the dense phase evaporates to vapor, and the flow becomes two-phase. A similar scenario can be encountered in the CO_2 supersonic ejector. As the supercritical CO_2 expands in the motive nozzle, flashing occurs near the throat and finally two-phase flow jets out at the outlet. To predict the flow behavior during the depressurization, a 100 m tube filled with CO_2 at p = 10 MPa, T = 300 K (supercritical state) is simulated. The tube is depicted in Figure 16. The pressure at the right boundary is fixed at 3 MPa. A grid composed of 1000 mesh points is used.



Figure 16. Schematic of the depressurization. The full tube is filled with supercritical CO_2 at 10 MPa, and the pressure at the right boundary is fixed to 3 MPa.

10 Pressure [MPa] 8 6 4 20 80 100 0 40 60
 300

 Temperature [K]

 280

 270
 270 20 40 60 80 100 Ó 1.0 8.0 6.0 6.4 0.4 **:-×. 0.2 80.0 82.5 85.0 87.5 90.0 92.5 95.0 97.5 100.0 *x* [m] ----- current work - Giliarhus et al. (2012) Hammer et al. (2013)

Figure 17. Comparisons to the numerical results of Giljarhus et al.²¹ and Hammer et al.¹¹ in terms of pressure, temperature, and liquid mass fraction distribution in the streamwise direction. Numerical data source: Giljarhus et al.²¹ and Hammer et al.¹¹



Figure 18. Comparison between the present numerical results and those of Hammer et al.¹¹ in terms of pressure, temperature, and liquid mass fraction for the depressurization. Numerical data from Hammer et al.¹¹



Figure 19. Streamwise distribution of pressure, density, velocity, and speed of sound along the tube using different EoSs.

At t = 0, the right side is opened and the supercritical CO₂ is exposed to the low pressure environment. Two types of expansion wave are generated and propagate to the left side. One is the expansion wave with the supercritical CO₂, and the other one is the evaporation front where the CO₂ vapor is created. The detailed discussion of these two types of expansion waves are found in ref 18. Similar phenomenon has been also observed and discussed for water.^{63,64} Figure 17 displays the distribution of the pressure, temperature, and liquid mass fraction along the tube at t = 0.2 s. Note that the x axis for the liquid mass fraction is presented only from 75 m to 100 m. The current results are compared to those of Giljarhus et al.²¹ and Hammer et al.¹¹ A good agreement with the results of Hammer et al.¹¹ is observed in Figure 17 and Figure 18. The results of Giljarhus et al.²¹ present some discrepancies at the location of the evaporation front. It could come from the different orders of the numerical scheme. Hammer et al.¹¹ used the MUSCL-FORCE scheme which is also second-order accurate, while the MUSTA used by Giljarhus et al.²¹ is first-order accurate. The liquid mass fraction, pressure, and temperature profiles in Figure 17 show that the discontinuities are better captured by the CLAWPACK solver.

Figure 18 shows comparisons in terms of density, velocity, and speed of sound between the results of Hammer et al.¹¹ and the current results. It is observed that the proposed formulation of the two-phase speed of sound from the HEM agrees with the results of Hammer et al.¹¹ who used the formulation derived by Flåtten and Lund.⁴⁴ Both formulations predict a discontinuity between the liquid and vapor phase (across the saturation curve), which is a feature of the HEM (see Figure 4).

5.3. Comparison between Different EoS and Speed-up Factor. The 1D classical shock tube problem is performed using the ClAWPACK solver to compare the Peng–Robinson EoS, the Stiffened Gas EoS, and the original Span-Wagner EoS with the proposed tabulated EoS. Only the vapor phase is considered in the simulations, because the Peng-Robison EoS is not appropriate for liquid and two-phase states. The accuracy of the results and the computational time are compared among the different EoSs in order to assess the performance of the tabulated EoS. Similarly as in Figure 14, a 1 m tube is considered. CO₂ with $\rho_{\rm L} = 85.31 \text{ kg} \cdot \text{m}^{-3}$, $T_{\rm L} = 360 \text{ K}$, $u_{\rm L} = 0 \text{ ms}^{-1}$ fills the left part whereas CO₂ with $\rho_{\rm R} = 15.1 \text{ kg} \cdot \text{m}^{-3}$, $T_{\rm R} = 360 \text{ K}$, $u_{\rm R} = 0 \text{ ms}^{-1}$ fills the right part, where the pressure is

computed by a different EoS. The subscripts L, R represent the left and right states, respectively. The theoretical formulation and the implementation details for the Peng-Robinson EoS and the Stiffened Gas EoS^{19,65} are presented in Appendix B. The numerical results are reported in Figure 19. The figure shows that the results using the original Span-Wagner EoS and that using the tabulated EoS agree perfectly. This validates the quality of the tabulated EoS. The speed of sound of the SG EoS differs from that of SW EoS. This EoS depends strongly on some parameters (presented in eq 14 in Appendix B). These parameters are computed by the user with a reference state. Here, a state between 5 PMa and 1 MPa is chosen as the reference state to better calibrate the density. PR EoS exhibits also some discrepancies in terms of pressure in the highpressure region and in terms of velocity at the contact surface. The computational time and speed-up are summarized in Table 2. All computations are carried out using a Intel core i7 with 8G

Table 2. Computational Time and Speed-up for Different EoSs. The Physical Time Is at 1.5 ms for the Shock Tube Problem

CPU time	ratio = $t_{\rm ref}/t$
1.67	66.16
3.35	32.98
0.85	129.9
110.49	1.0
	CPU time 1.67 3.35 0.85 110.49

memory. The original Span-Wagner EoS is considered as the reference, thus its CPU time is considered as the reference time $t_{\rm ref}$. The speed-up is the ratio between the reference CPU time and the CPU time taken by other EoSs ($t_{\rm ref}/t$). The tabulated EoS is 66 times faster than the original SW EoS and produces undistinguishable results, as shown in Figure 19. It is also 2 times faster than the PR EoS which is not appropriate to describe the liquid and two-phase properties as well. The SG EoS is the fastest one but it is parameter-dependent. This limits the use of SG EoS for large variation of phase states. Additionally, the SG EoS computes the properties with a linear form around the reference state. Thus, for phase states close to the critical point where large nonlinear variation of the properties can be encountered, the SG EoS is not appropriate. This is the case for the two-phase CO₂ ejector in refrigeration,



Figure 20. Converging–diverging nozzle geometry which the total length is 83.50 mm and the diverging angle is 0.612° , the same as that investigated by Nakagawa et al.⁶

for which the operating conditions are near the critical point.^{4,32} Therefore, this tabulated EoS exhibits some advantages in terms of high accuracy and high efficiency and it is appropriate for future massive CFD simulations.

5.4. 2D Converging–Diverging Nozzle. In this section, a two-phase CO₂ converging-diverging nozzle is investigated. Such a converging-diverging nozzle can be used as the motive nozzle in a supersonic ejector that replaces the expansion valve in a refrigeration cycle. It has been proven that the flow condition in the motive nozzle has strong effects for the efficiency of the ejector and the refrigeration cycle.⁴ It was noticed that flashing and two-phase shock waves could occur in the converging-diverging nozzle and change completely the flow feature at the outlet of the nozzle.⁸ This nozzle has been studied by Nakagawa et al.⁶ and it is investigated by the current numerical model. The structured mesh is made of 50 000 nodes in the whole 2D computational domain. The total length of the nozzle is 83.50 mm and the diverging angle is 0.612° as presented in Figure 20. The inlet conditions are p = 9.1 MPa and T = 309.65 K, while at the outlet, the pressure is about 0.5 MPa. CO₂ is supercritical at inlet and two-phase state at outlet. The flow reaches sonic conditions near the throat and accelerates until Ma = 2 at the outlet; no shock forms in the nozzle.

The measurements of the pressure from strain gauges and obtained by the saturation temperature in the diverging part, were achieved by Nakagawa et al.⁶ These results are used to validate the current 2D simulation, reported in Figure 21. For the current two-phase model, HEM considers that the two phases are in thermodynamic and mechanical equilibrium



Figure 21. Pressure profile along the center line of the nozzle, comparing with pressure measurements by Nakagawa et al.⁶ Experimental data from Nakagawa et al.⁶

without body forces and viscous effects. Thus, the current results do not consider the viscous dissipation and the thermodynamic nonequilibrium. These could be the explanation of the little differences of the pressure near the throat. Indeed the measurements of the pressure away from the throat, where equilibrium is more likely to occur, tend to agree well with the numerical results. This means that the flows are in thermodynamic and mechanical equilibrium and the HEM can correctly predict the flow behavior. Furthermore, to determine which effects play a more important role for the flow in the nozzle, a more complete model is needed which considered the viscous effects, the nonequilibrium effects, and the turbulence. In addition, more measurements of the pressure are also expected to give an exact pressure profile in the nozzle, because it is believed that extracting pressure from the wall temperature could induce wrong values and misinterpretation of the thermo-equilibrium level. These are beyond the main objective of this paper. Figure 22 displays the Mach number and the vapor quality on the 2D map of the nozzle. It is observed that the vapor quality changes from 0 to 0.3 at the throat, which indicates the location of the flashing, thus the flow becomes a two-phase flow in the diverging part. The vapor quality continues to increase up to 0.5 at the outlet of the nozzle. The Mach number map shows that the flow becomes sonic right at the throat and at the outlet it attains a value Ma = 2; the flow is fully supersonic.

6. CONCLUSION

A look-up table method based on the Span-Wagner EoS is presented in this paper. This EoS is indeed considered as the international standard EoS for CO₂. The proposed tabulated EoS can provide CO₂ properties from the triple-point temperature to 500 K with the pressure up to 50 MPa, covering a sufficiently large property range for industrial applications. These two-phase properties are implemented and used on the Homogeneous Equilibrium Model (HEM). The internal energy and the specific volume are chosen as the two dependent variables, which simplifies the coupling with any CFD code in the conservative formulation. A series of numerical experiments has been performed to assess the performance of the tabulated EoS in terms of accuracy and efficiency. The numerical simulations are done easily by the CLAWPACK solver. First, a classical single-phase shock tube problem is simulated, and the results agree perfectly with those of Giljarhus et al.²¹ Second, a depressurization problem is investigated. The results show that the tabulated EoS can achieve a good accuracy for two-phase and supercritical CO₂ simulations. The proposed approach exhibits very good features in terms of accuracy, and a very significant gain in terms of computational time for future massive CFD simulations. Then,



Figure 22. Vapor quality and Mach number map from 20 mm to 80 mm.

the different available EoSs for CO_2 , such as the Peng– Robinson, the Stiffened-Gas, and the original Span-Wagner EoS are compared to the tabulated EoS. The proposed EoS exhibits very good features in terms of accuracy, and a very significant gain in terms of computational time for future massive CFD simulations. Finally, a 2D simulation of the two-phase CO_2 converging–diverging nozzle is carried out. The present numerical results show a rather good agreement with the experimental measurements, but there are still some discrepancies, due to the choice of the physical model (inviscid, HEM). Therefore, more complete investigations are expected by considering the viscosity, the nonequilibrium effects, the turbulence, and 3D effects.

In summary, this tabulated EoS exhibits the following advantages:

- Accuracy and efficiency: it can be used for massive CFD simulations such as 3D two-phase LES.
- Flexibility: it can be adapted to various two-phase models, such as HEM, HRM (Homogeneous Relaxation Model), etc.
- Stability: for numerical simulations of two-phase, and supercritical CO₂ flows.
- The location of the phase state in the e-v space can be determined. Thus, the phase states in the whole computational domain can be monitored during the simulation.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b00507.

Appendix A, speed of sound in the HEM; Appendix B, theoretical formulations of EoS and implementations in CLAWPACK; Appendix C, nomenclature (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: yu.fang@uclouvain.be.

ORCID 💿

Yu Fang: 0000-0002-7872-3271

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Yu Fang and Sébastien Poncet acknowledge the support of the NSERC chair on industrial energy efficiency established in 2014 at Université de Sherbrooke funded by Hydro-Québec, Natural Resources Canada (CanmetEnergy-Varennes) and Rio Tinto Alcan. Computational resources have been provided by Compute Canada and the Consortium des Équipements de Calcul Intensif (CÉCI), funded by the Fonds de la Recherche Scientifique de Belgique (F.R.S.-FNRS) under Grant No. 2.5020.11

REFERENCES

(1) Bai, T.; Yan, G.; Yu, J. Performance of a new two-stage multiintercooling transcritical CO_2 ejector refrigeration cycle. *Int. J. Refrig.* **2015**, 58, 22–34.

(2) Li, D.; Groll, E. D. Transcritical CO_2 refrigeration cycle with ejector-expansion device. *Int. J. Refrig.* **2005**, *28*, 766–773.

(3) Elbel, S. Historical and present developments of ejector refrigeration systems with emphasis on transcritical carbon dioxide air-conditioning applications. *Int. J. Refrig.* **2011**, *34*, 1545–1561.

(4) Elbel, S.; Hrnjak, P. Experimental validation of a prototype ejector designed to reduce throttling losses encountered in transcritical R744 system operation. *Int. J. Refrig.* **2008**, *31*, 411–422.

(5) Marynowski, T.; Desevaux, P.; Mercadier, Y. Experimental and numerical visualisations of condensation process in supersonic ejector. *J. Visualization* **2009**, *12*, 251–258.

(6) Nakagawa, M.; Berana, M. S.; Kishine, A. Supersonic two-phase flow of CO_2 through converging-diverging nozzles for the ejector refrigeration cycles. *Int. J. Refrig.* **2009**, *32*, 1195–1202.

(7) Nakagawa, M.; Berana, M. S.; Harada, A. Shock waves in supersonic two-phase flow of CO_2 in converging-diverging nozzles. International Refrigeration and Air Conditioning Conference, Purdue, USA, 2008.

(8) Berana, M.; Nakagawa, M.; Harada, A. Shock waves in supersonic two-phase flow of CO_2 converging-diverging nozzles. *HVACR Res.* **2009**, 15, 1080–1098.

(9) Xu, B. P.; Jie, H. G.; Wen, J. X. Numerical study of compressed CO_2 pipeline decompression characteristics using CFD-DECOM. *IChemE Symp. Ser. no.* 156 **2011**, 22, 347–355.

(10) Morin, A.; Aursand, P. K.; Flätten, T.; Munkejord, S. T. Numerical resolution of CO_2 transport dynamics. Proceedings of SIAM Conference Mathematics for Industry: Challenges and Frontiers (MI09). San Francisco, USA, October 9–10, 2009.

(11) Hammer, M.; Ervik, A.; Munkejord, S. Method using a densityenergy state function with a reference equation of state for fluiddynamic of vapor-liquid-solid carbon dioxide. *Ind. Eng. Chem. Res.* **2013**, *52*, 9965–9978.

(12) Nordhagen, H. O.; Kragset, S.; Berstad, T.; Morin, A.; Dørum, C.; Munkejord, S. T. A new coupled fluid-structure modelling methodology for running ductile fracture. *Comput. Struct.* **2012**, 9495, 13–21.

(13) Lees, F. P. Lees' Loss Prevention in the Process Industries: Hazard Identification, Assessment and Control; Butterworth-Heinemann: UK, 1996.

(14) Pohanish, P.; Greene, S. Hazardous Materials Handbook: Carbon Dioxide; Van Nostrand Reinhold: USA, 1996.

(15) Raman, S. K.; Kim, H. D. Solutions of supercritical CO_2 flow through a converging-diverging nozzle with real gas effects. *Int. J. Heat Mass Transfer* **2018**, *116*, 127–135.

(16) Aidoun, Z.; Ouzzane, M. The effect of operating conditions on the performance of a supersonic ejector for refrigeration. *Int. J. Refrig.* **2004**, *27*, 974–984.

(17) Smolka, J.; Bulinski, Z.; Fic, A.; Nowak, A.; Banasiak, K.; Hafner, A. A computational model of transcritical R744 ejector based on a homogeneous real fluid approach. *Appl. Math. Model* **2013**, *37*, 1208–1224.

(18) Lund, H.; Flåtten, T.; Munkejord, S. Depressurization of carbon dioxide in pipelines - models and methods. *Energy Procedia* **2011**, *4*, 2984–2991.

(19) Métayer, O.; Massoni, J.; Saurel, R. Elaboration equation of state of a liquid and its vapor for two-phase flow models. *Int. J. Therm. Sci.* **2004**, 43, 265–276.

(20) Brown, S.; Martynov, S.; Mahgerefteh, H.; Chen, S.; Zhang, Y. Modelling the non-equilibrium two-phase flow during depressurisation of *CO*₂ pipelines. *Int. J. Greenhouse Gas Control* **2014**, *30*, 9–18.

(21) Giljarhus, K. E. T.; Munkejord, S. T.; Skaugen, G. Solution of the Span-Wagner equation of state using a density-energy state function for fluid-dynamic simulation of carbon dioxide. *Ind. Eng. Chem. Res.* **2012**, *51*, 1006–1014.

(22) Yazdani, M.; Abbas, A.; Radcliff, T. Numerical modelling of twophase supersonic ejectors for work-recovery applications. *Int. J. Heat Mass Transfer* **2012**, *55*, 5744–5753.

(23) Colarossi, M.; Trask, N.; Schmidt, D.; Bergander, M. Multidimensional modelling of condension two-phase ejector flow. *Int. J. Refrig.* **2012**, *35*, 290–299.

(24) Lemmon, E. W.; Huber, M. L.; McLinden, M. NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties; REFPROP. NIST: Gaithersburg, USA, 2010.

(25) Span, R.; Wagner, W. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **1994**, *25*, 1509–1596.

(26) Bell, I. H.; Wronski, J.; Quoilin, S.; Lemort, V. Pure and Pseudopure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Property Library CoolProp. *Ind. Eng. Chem. Res.* **2014**, 53, 2498–2508.

(27) De Lorenzo, M.; Lafon, P.; Di Matteo, M.; Pelanti, M.; Seynhaeve, J. M.; Bartosiewicz, Y. Homogeneous two-phase flow models and accurate steam-water table look-up method for fast transient simulations. *Int. J. Multiphase Flow* **2017**, *95*, 199–219.

(28) Kunick, M.; Kretzschmar, H. J.; Gampe, U. Fast calculation of thermodynamic properties of water and steam in process modelling using spline interpolation. Proceedings of the 15th International Conference on the Properties of Water and Steam. Berlin, Germany, September 7–11, 2008.

(29) Khatami, F.; Weide, E. V. D.; Hoeijmakers, H. Multiphase thermodynamic tables for efficient numerical simulation of cavitating flows: A novel Look-up approach toward efficient and accurate tables. *Heat Transfer Eng.* **2015**, *36*, 1065–1083.

(30) Brown, S.; Peristeras, L.; Martynov, S.; Porter, R.; Mahgerefteh, H.; Nikolaidis, I. K.; Boulougouris, G. C.; Tsangaris, D. M.; Economou, I. G. Thermodynamic interpolation for the simulation of two-phase flow of non-ideal mixtures. *Comput. Chem. Eng.* **2016**, *95*, 49–57.

(31) Gross, J.; Sadowski, G. Perturbed-chain SAFT: an equation of state based on a perturbation theory for chain molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244–1260.

(32) Ameli, A.; Afzalifar, A.; Turunen-Saaresti, T. Non-equilibrium condensation of supercritical carbon dioxide in a converging-diverging nozzle. *J. Phys.: Conf. Ser.* **2017**, *821*, 012–025.

(33) Giacomelli, F.; Mazzelli, F.; Milazzo, A. Evaporation in supersonic CO_2 ejectors: analysis of theoretical and numerical models. 9th International Conference on Multiphase Flow, Firenze, Italy, May 22–27, 2016.

(34) Bilicki, Z.; Kestin, J. Physical aspects of the relaxation model in two-phase flow. *Proc. R. Soc. London, Ser. A* **1990**, *428*, 379–397.

(35) Bartosiewicz, Y.; Seynhaeve, J. Delayed equilibrium model (DEM) of flashing choked flows relevant to LOCA. *Multiphase Sci. Technol.* **2013**, *25*, 117–131.

(36) LeVeque, R. J.; Berger, M. J. Clawpack software, version 4.3; Clawpack Development Team, 2017; http://www.clawpack.org.

(37) LeVeque, R. J. Finite Vol. Methods for Hyperbolic Problems; Cambridge University Press: Cambridge, UK, 2002.

(38) Toro, E. F.; Spruce, M.; Speares, W. Restoration of the contact surface in the HLL Riemann solver. *Shock Waves* **1994**, *4*, 25–34.

(39) Baer, M. R.; Nunziato, J. W. A two-phase mixture theory for the deflagration-to-detonation transition (ddt) in reactive granular materials. *Int. J. Multiphase Flow* **1986**, *12*, 861–889.

(40) Pelanti, M.; Shyue, K.-M. A mixture-energy-consistent sixequation two-phase numerical model for fluids with interfaces, cavitation and evaporation waves. *J. Comput. Phys.* **2014**, *259*, 331– 357.

(41) Saurel, R.; Petitpas, E.; Berry, R. A. Simple and efficient relaxation methods for interfaces separating compressible fluids, cavitating flows and shocks in multiphase mixture. *J. Comput. Phys.* **2009**, *228*, 1678–1772.

(42) Mazzelli, F.; Little, A.; Garimella, S.; Bartosiewicz, Y. Condensation in supersonic steam ejectors: comparison of theoretical and numerical models. 9th International Conference on Multiphase Flow, Firenze, Italy, May 22–27, 2016.

(43) Yang, Y.; Shen, S. Q. Numerical simulation on non-equilibrium spontaneous condensation in supersonic steam flow. *Int. Commun. Heat Mass Transfer* **2009**, *36*, 902–907.

(44) Flåtten, T.; Lund, H. Relaxation two-phase flow models and the subcharacteristic conditions. *Math. Models Methods Appl. Sci.* **2012**, *21*, 2374–2407.

(45) Lucas, C.; Rusche, H.; Schroeder, A.; Koehler, J. Numerical investigation of a two-phase CO_2 ejector. *Int. J. Refrig.* **2014**, 43, 154–166.

(46) Palacz, M.; Smolka, J.; Fic, A.; Bulinski, Z.; Nowak, A.; Banasiak, K.; Hafner, A. Application range of the HEM approach for CO_2 expansion inside two-phase ejectors for supermarket refrigeration systems. *Int. J. Refrig.* **2015**, *59*, 251–258.

(47) Palacz, M.; Haida, M.; Smolka, J.; Nowak, A.; Banasiak, K.; Hafner, A. HEM and HRM accuracy comparison for the simulation of CO_2 expansion in two-phase ejectors for supermarket refrigeration systems. *Appl. Therm. Eng.* **2016**, *115*, 160–169.

(48) Wood, A. A. A Textbook of Sound; G. Bell and Sons: London, UK, 1964.

(49) Ameur, K.; Aidoun, Z.; Ouzzane, M. Modeling and numerical approach for the design and operation of two-phase ejectors. *Appl. Therm. Eng.* **2016**, *109*, 809–818.

(50) Nakagawa, M.; Harada, A.; Berana, M. S. Analysis of expansion waves appearing in the outlets of two-phase flow nozzles. *HVACR Res.* **2009**, *15*, 1065–1079.

(51) Faccanoni, G.; Kokh, S.; Allaire, G. Approximation of liquidvapor phase transition for compressible fluids with tabulated EOS. *C. R. Acad. Sci. Paris, Ser. I* **2010**, *348*, 473–478.

(52) RELAP5/MOD3.3, Code Manuel; Information Systems Laboratories, Inc: Idaho Falls, USA, 2001.

(53) Tiselj, I.; Horvat, A.; Gale, J. Numerical scheme of the WAHA code. *Multiphase Sci. Technol.* **2008**, *20*, 323–354.

(54) Hughes, T. J. R. *The Finite Element Method:Linear Static and Dynamic Finite Element Analysis;* Dover Publications: New Jersey, USA, 2000.

(55) Ruas, V. Numerical Methods for Partial Differential Equations: An Introduction; Wiley: New-York, USA, 2016.

(56) Swesty, F. D. Thermodynamically consistent interpolation for equation of state tables. *J. Comput. Phys.* **1996**, *127*, 118–127.

(57) Godunov, S. A difference method for numerical calculation of discontinuous solutions of the equations of hydrodynamics. *Mater. Sb.* **1959**, 47, 271–306.

(58) Toro, E. F. Riemann Solvers and Numerical Methods for Fluids Dynamics; Springer-Verlag: Berlin, Heidelberg, Germany, 1997.

(59) Davis, S. F. Simplified second-order Godunov-type methods. SIAM J. Sci. Stat. Comput. 1988, 9, 445-473.

(60) LeVeque, R. J. Wave propagation algorithms for multidimensional hyperbolic systems. J. Comput. Phys. **1997**, 131, 327–353.

(61) Toro, E. F.; Titarev, V. A. MUSTA fluxes for systems of conservation laws. J. Comput. Phys. 2006, 216, 403-429.

(62) Titarev, V. A.; Toro, E. F. MUSTA schemes for multidimensional hyperbolic systems: analysis and improvements. *Int. J. Numer. Methods Fluids* **2005**, *49*, 117–147.

(63) Saurel, R.; Petitpas, E.; Abgrall, R. Modelling phase transition in metastable liquids: application to cavitating and flashing flows. *J. Fluid Mech.* **2008**, *607*, 313–350.

(64) Dumbser, M.; Iben, U.; Munz, C.-D. Efficient implementation of high order unstructured WENO schemes for cavitating flows. *Comput. Fluids* **2013**, *86*, 141–168.

(65) Flåtten, T.; Morin, A.; Munkejord, S. T. On solutions to equilibrium problems for systems of stiffened gases. *SIAM J. Appl. Math.* **2011**, *71*, 41–67.