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Flash calculations with specified entropy and stagnation enthalpy

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ABSTRACT

Finding the properties of a stream leaking from a pressure vessel, assuming it is in thermodynamic equilibrium, requires the solution of a phase equilibrium problem with known values of component amounts, entropy, and stagnation enthalpy. If part of dynamic simulations of leaking vessels, these calculations need to be executed hundreds or thousands of times. Ideally, they should be fast and never fail, even when executed for difficult conditions, such as high pressure systems close to phase boundaries or to critical points. This paper proposes a single loop algorithm to solve flash problems with specified values of entropy and stagnation enthalpy. The results show that it is much faster than a nested loop algorithm for the same purpose, but occasionally fails to converge especially very close to phase boundaries. The nested loop algorithm succeeded in these situations however at large computational cost because of multiple phase additions and removals during the course of the iterations. A satisfactory balance of speed and reliability was obtained by favoring the single loop algorithm but, when it fails, using the nested loop algorithm as a backup procedure.

1. Introduction

Flash calculations are key elements in the simulation of chemical processes and the focus of many researchers who endeavor to devise reliable and efficient algorithms. For given amounts of each component, the specifications of temperature and pressure ($TP\underline{n}$ flash) (e.g., Ref. [1,2]), enthalpy and pressure ($HP\underline{n}$ flash) (e.g., Ref. [3]), and entropy and pressure ($SP\underline{n}$ flash) (e.g., Ref. [3]) are the most common in steady-state simulations. The $TP\underline{n}$ flash is often used to predict the performance of isothermal separators, the $HP\underline{n}$ flash is used for modeling adiabatic separators and throttling processes, and the $SP\underline{n}$ flash is useful for the preliminary design of compressors and turbines under the assumption of adiabatic and reversible operation. Volume-based calculations [4] and flash specifications are also relevant in a number of applications. The flash calculation with specification of temperature and volume ($TV\underline{n}$ flash) (e.g., Ref. [5]) is useful to determine the state of a fluid within a storage vessel, and with specification of internal energy and volume ($UV\underline{n}$ flash) [6,7] is suitable to find the state of a fluid during the dynamic simulation of vessels.

One approach to these problems is to formulate a set of nonlinear algebraic equations whose solution characterizes the equilibrium state. Another is to formulate each of them as the minimization, or maximization, of a thermodynamic function. The latter approach has the following advantages: (a) by checking the value of the objective function, one can unequivocally monitor the progress toward the solution; (b) this progress is guaranteed if the numerical minimization (maximization) method used never allows an increase (decrease) in the objective function from one iteration to the next [2]; (c) the Hessian matrix is necessarily symmetrical, unlike the Jacobian matrix of the nonlinear set of equations. Because of symmetry, only the lower or upper triangular part of the Hessian matrix needs to be evaluated, which contributes to reducing the computational effort.

There are, however, flash problems that cannot be formulated as finding the extreme value of a thermodynamic function [8]. This paper focuses on one of them: the $H_{st}S\underline{n}$ flash, i.e., with specification of entropy and stagnation enthalpy (H_{st}), which is the summation of the enthalpy and kinetic energy. Two applications illustrate its relevance. The first of them is the simulation of converging–diverging (CD) nozzles, which have been proposed as a method to remove impurities from light gas mixtures, such as natural gases. At least one company, Twister BV, manufactures devices for such applications. These nozzles are designed in such a way that the flow is sonic at the nozzle's throat, i.e., its location of minimum cross sectional area, and supersonic in part of the diverging section. The typical steady-state energy balance in a unit like that neglects changes in potential energy, but changes in

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kinetic energy need to be considered because of the high fluid speeds involved. If one assumes that the CD nozzle is adiabatic, then what essentially remains is that the stagnation enthalpy is constant along the nozzle. Another approximation in preliminary calculations for these devices is to assume that the flow is adiabatic and reversible between the nozzle's entrance and the point where a shock wave occurs, generally inside the nozzle in its diverging section [9]. The second application is the prediction of the thermodynamic properties, fluid speeds, and flow rates of streams leaked or vented from a pressure vessel, all of which are important to predict the consequences of industrial accidents. In such events, the fluid may have more than one phase at the exit point and it is necessary to find the thermodynamic sound speed [10–12] to determine whether the flow is choked or not. Sound speeds of liquids and vapors can be substantially different and their prediction in systems with more than one phase has many steps, which require knowledge of the temperature, phase volumes, and phase amounts and compositions. One approach to such calculations is to assume that the region inside the vessel next to the fluid's exit point is a hypothetical converging nozzle that operates adiabatically and reversibly, i.e., isentropically. This set of assumptions also leads to a problem in which the stagnation enthalpy and entropy are fixed. Despite its practical importance, no specialized algorithm for this flash specification with non-ideal fluids could be found in the literature.

It is possible to solve the $H_{st}S\underline{n}$ flash problem using nested loops by, for example, solving a $SP\underline{n}$ flash in the inner loop and using the energy balance to update the fluid pressure in the outer loop, among several other possibilities. Implemented in a dynamic simulator of leaks and venting operations [13,14], this sort of nested procedure has shown to be reliable but slow. Such simulations typically require the execution of hundreds or thousands of $H_{st}S\underline{n}$ flash calculations. Therefore, it is desirable that the computational procedure be both reliable and fast, and speed was the drive to develop the single-loop algorithm proposed in this work. Indeed, the results show that the single-loop algorithm is much faster than the nested-loop one, but its numerical convergence is also more sensitive to the quality of the initial estimates. A good compromise was to implement a hybrid scheme that favors the single-loop procedure which, when it fails to converge, activates the nested-loop algorithm as a backup.

The emphasis of this paper is on a vessel with a discharge of fluid, whose speed at the exit point of the hypothetical converging nozzle is either subsonic or sonic. The next section presents the formulations for these two cases, followed by sections that discuss the criteria adopted for phase addition and removal during the course of the iterative procedure and implementation details. The results section shows examples of systems with one, two, and three phases and compares the computational effort of the single and nested loop algorithms. The paper ends with the conclusions of this research work.

2. Approach and formulation

The general approach adopted to solve the $H_{st}S\underline{n}$ flash is to add phases to the system gradually, as needed, by applying the global phase stability test. The removal of phases whose amounts become very small during the course of the iterations is also an integral part of the calculation procedure.

As the near-term goal of our research was to develop an algorithm suitable to run as an element of a simulator of leaks from pressure vessels, the focus is on specifications relevant to the modeling of a converging nozzle. The starting point of the formulation is to consider two locations along such a nozzle, whose operation is assumed to be adiabatic and reversible, therefore isentropic, and at steady-state. For convenience, it is assumed hereafter that the conditions at the upstream location are known and that the goal is to determine the conditions at the downstream location, which may have one or more phases. The fluid mixture is non-reactive and, therefore, the total number of moles (n_T) passing by the two locations per unit of time is identical. In the formulations that follow, changes in potential energy are neglected.

Two situations for the fluid speed are considered: (1) subsonic and (2) equal to the thermodynamic sound speed, which is the maximum speed achievable in a converging nozzle.

2.1. Subsonic flow

Assuming that the fluid speed is unconstrained, the energy balance is:

$$f_1 = \left[n_T M \frac{u^2}{2} + \sum_{j=1}^{n_p} H_j\left(T, V_j, \underline{n}_j\right) \right] - \left[n_T M \frac{u_{in}^2}{2} + \sum_{j=1}^{n_{p,in}} H_j\left(T_{in}, V_{in,j}, \underline{n}_j\right) \right] = 0 \tag{1}$$

where the subscript *in* denotes properties of the input stream, which are all known. The properties of the output stream have no subscript in order to alleviate the notation. In Eq. (1), T is the absolute temperature, V_j and H_j are the volume and enthalpy of phase j, and $\underline{n}_j$ represents the set of mole numbers of all components in phase j, M is the molar mass, which is the same in the input and output streams. The symbol u denotes the fluid velocity, n_p is the number of phases in the output stream, and $n_{p,in}$ is its counterpart for the input stream.

The mechanical equilibrium condition is such that the pressure of the all the phases present at the exit point are equal:

$$f_{2,j} = -P_j + P_B = 0 \tag{2}$$

where P_j is the pressure in phase j at the exit point. In addition, the pressures of all these phases are equal to the backpressure, P_B, which is the environmental pressure away from the nozzle.

The isentropic condition is:

$$f_3 = \sum_{j=1}^{n_p} S_j\left(T,\ V_j,\ \underline{n}_j\right) - \sum_{j=1}^{n_{p,\ in}} S_j\left(T_{in},\ V_{in,\ j},\ \underline{n}_j\right) = 0 \tag{3}$$

where S_j is the entropy of phase j.

The phase equilibrium equations are:

$$f_{4,\ ij} = n_i(\mu_{ij} - \mu_{iJ}) = 0 \tag{4}$$

which holds for each component i. The symbols μ_{ij} and μ_{iJ} are the chemical potential of component i in phase j and in phase J. For numerical convenience, J refers to the phase with the largest amount of component i at any given iteration. The mole numbers of component i multiplies the difference of chemical potentials, also for numerical convenience. With this formulation and the choice of independent variables adopted in this work, a large portion of the Jacobian matrix is symmetrical (Eq. (A.16)), thereby reducing the computational load for its evaluation.

These equations make up a set of $(2 + n_p + n_c(n_p - 1))$ equations. Several solution procedures are possible. One of them is impose from the beginning of the calculations that the pressure in all phases is the backpressure, which is equivalent to solving Eq. (2). The subsequent step is to solve Eqs. (1–4), to determine T, u, and the