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A Non-equilibrium Approach to Model Flash Dynamics with Interface Transport

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Abstract: This paper presents a modeling approach for a class of multiphase chemical systems, based on non-equilibrium thermodynamics, specialized to an open flash-drum system. A compartmental model is considered to establish the dynamics of the gas and liquid phases, while a model of interface transport yields to constraints in the model. The overall system is thus written as a Differential-Algebraic system of Equations (DAE). The derived model is shown to be of index one, for which a stability analysis, based on Lyapunov first method, is briefly developed. An example is presented to illustrate the proposed modeling and stability analysis approach, together with numerical simulations.

Keywords: Non-equilibrium thermodynamics, Irreversible thermodynamics, Multiphase systems, Differential-algebraic nonlinear systems, Flash-drum dynamics, Lyapunov stability

1. INTRODUCTION

Despite historical and contemporary significance, design, operation and control of distillation processes have proven to be difficult tasks (Skogestad, 1997; Taylor and Krishna, 2000). Analysis and model-based feedback control design for multiphase chemical systems are still challenging problems. In this article, we explore the possibility of modeling a special case of multiphase systems, the open flash-drum, using a physics-based non-equilibrium thermodynamic model. In contrast with traditional equilibrium formulations, non-equilibrium models are capable of tracking irreversible phenomena such as entropy production and energy degradation (de Groot and Mazur, 1984). Modeling techniques taking into account irreversible phenomena have led to useful insights for stability analysis and feedback control design in the chemical process systems literature (Alonso and Ydstie, 1996; Ydstie and Alonso, 1997; Favache and Dochain, 2009; García-Sandoval et al., 2015; Ydstie, 2016).

A key theory used in the analysis and control of physical systems was originally developed by Willems (1972) who proposed dissipative systems theory as an extension of classical (linear) passivity-based analysis. Dissipative systems analysis has been established as a practical tool for analysis and control design of mechanical and electrical systems. As for chemical process systems, thermodynamic-based dissipative systems theory has received an increasing level of attention in the literature. Ydstie and Alonso (1997) introduced the concept of dissipativity for chemical process systems using the first and second laws of thermodynamics. Favache and Dochain (2009) explored the possibility of characterizing the continuous stirred tank reactor through energetic and entropic formulations with insightful results. These studies, and most of the literature on applications of dissipative systems theory to chemical process systems, focus on simple thermodynamic systems, in particular single-phase homogeneous systems. Studies on complex composite processes, for example multiphase systems, are still unexplored from a physics-based analysis perspective.

The study of multiphase processes from a system perspective can be traced back to the pioneering work of Rosenbrock (1963), who demonstrated that a non-ideal binary distillation column operates at a unique asymptotically stable steady state. Based on geometric considerations, Rouchon and Creff (1993) developed stability analysis for a multicomponent flash-drum. Unfortunately, this approach does not extend to multistage process units. A more recent contribution can be found in the work of Ydstie (2016), where conditions for the existence of a unique stable steady-state for an adiabatic flash-drum were established. To the best of the authors knowledge, there are no results on the stability of multiphase chemical units far from equilibrium, in particular for open liquid-vapor process units exchanging mass and energy with the environment.

The absence of physics-based stability criteria for composite systems in the literature follows as a consequence of the convexity properties of thermodynamic potentials in multiphase processes. For a simple thermodynamic system, these potentials are convex functions of the extensive variables (Callen, 1985), as depicted in Figure 1 (left). Such convexity properties permit to assess for stability and to build control structures using dissipative systems theory, as proposed by Favache and Dochain (2009) and García-Sandoval et al. (2015). The convexity properties are lost however when considering composite thermodynamic systems and systems going through phase changes (Gromov and Caines, 2015). The existence of multiple phases follows as a consequence of the loss of convexity in thermodynamic potentials (Callen, 1985), see Figure 1 (right). We believe that one of the keys to develop stability criteria for multiphase processes lies in the non-convex nature of composite systems. To account for the loss of convexity for this class of systems, we propose to consider non-equilibrium thermodynamics to track the dynamical evolution of the system.

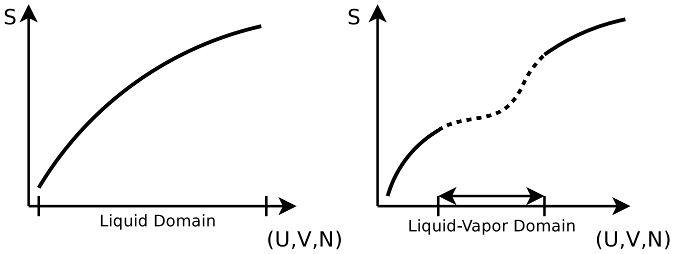

Fig. 1. Entropy for a liquid and a liquid-gas system.

Stationary non-equilibrium liquid-vapor systems were studied by Krishnamurthy and Taylor (1985) for modeling purposes. Their work considers a multiphase process globally far from equilibrium, where inhomogeneities between phases could arise. Each subsystem in their work (liquid phase, gas phase, and the interface) is considered to be locally at thermodynamic equilibrium. In this article, we present a model for a flash-drum evolving on a non-equilibrium manifold, extending the work of Krishnamurthy and Taylor (1985) to dynamic regimes. We then briefly discuss the stability of multiphase systems using the resulting model.

The paper is organized as follows. In Section 2, the non-equilibrium flash-drum differential-algebraic (DAE) model is presented considering mass and energy conservation principles for gas and liquid phases. The DAE model takes into account exchange processes through the interface, viewed as constraints on the dynamics. In Section 3, the linearized DAE is rewritten as a system of differential equations (ODE). Then, Lyapunov first method is proposed to characterize the stability of the ODE. A numerical example is presented in Section 4 for a non-ideal water-methanol liquid gas mixture. Results and future areas for research are discussed in Section 5.

2. FLASH-DRUM MODEL

In this section, a nonlinear differential algebraic system is built from conservation principles to describe the non-equilibrium flash-drum dynamics. The first postulate of thermodynamics (Callen, 1985) states that a system is completely characterized once the internal energy U, the volume V, and the mole numbers of each component N_j are set. In turn, when a system interacts with its surroundings, the state (U, V, N_j) evolves according to the first and second laws of thermodynamics. For open systems, these laws lead to nonlinear differential-algebraic systems (DAE systems) that describe the evolution of the physical properties for a system interacting with its surroundings (Bird et al., 2002; Sandler, 1999).

2.1 Conservation principles

Consider an open rigid flash-drum with c components, depicted in Figure 2. Mass and energy flow in and out between the system and the environment. In addition, mass and energy are exchanged between phases at rates e (J/sec) and n (mol/sec), respectively.

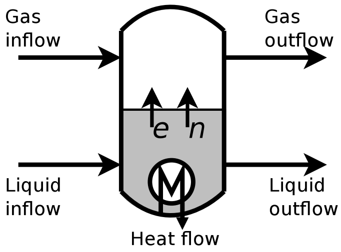

Fig. 2. Mass and energy flows in a flash-drum

For modeling purposes, the following assumptions are considered:

(i) Each phase is perfectly mixed;
(ii) No significant variations in potential energy occur in the system; and,
(iii) Compressibility and viscous effects are negligible.

Under the above assumptions, the liquid phase dynamics is described as

$$\dot{N}_{l,j} = F_{l,N_j,in} - N_{l,j}\frac{F_{l,V}}{V_l} - n_{l,j}\ , \quad j = \{1, ..., c-1, \Omega\} \tag{1a}$$

$$\dot{K}_l = F_{l,K,in} - K_l\frac{F_{l,V}}{V_l} - P_l\left(\dot{V} + F_{l,V}\right) - e_{l,K} \tag{1b}$$

$$\dot{U}_l = F_{l,U,in} - U_l\frac{F_{l,V}}{V_l} - e_{l,U}, \tag{1c}$$

similarly, the gas phase dynamics is given by

$$\dot{N}_{g,j} = F_{g,N_j,in} - N_{g,j}\frac{F_{g,V}}{V_g} + n_{g,j}\ , \quad j = \{1, ..., c-1, \Omega\} \tag{2a}$$

$$\dot{K}_g = F_{g,K,in} - K_g\frac{F_{g,V}}{V_g} - P_g\left(\dot{V} + F_{g,V}\right) + e_{g,K} \tag{2b}$$

$$\dot{U}_g = F_{g,U,in} - U_g\frac{F_{g,V}}{V_g} + e_{g,U}, \tag{2c}$$

where we have written $K = Mv^2/2$ for the kinetic energy in each flowing phase; $F_{N_j,in}, F_{K,in}, F_{U,in}$ for molar, mechanical and internal energy inflow rates; F_V for the volumetric outflow rates; P represents the pressure of each bulk phase; subscripts l and v refer to liquid and gas phases variables, respectively. The sub-index Ω is introduced to represent total amounts, and flow terms n_j, e_K, e_U represent the rate at which moles, kinetic and internal energy are transferred between phases.

The liquid holdup sets the volume space for each phase following

$$V_l = \sum_{j=1}^{c} \bar{V}_{l,j} N_{l,j} \tag{3a}$$

$$V_g = V_\Omega - V_l, \tag{3b}$$

where the total volume V_Ω is fixed by the size of the flash-drum and the partial molar volume of component j, $\bar{V}_{l,j}$, is a fixed thermodynamic parameter. The gas pressure is set using the generalized gas law

$$P_g = ZRC_gT_g, \tag{4a}$$

where Z corresponds to the compressibility factor of the gaseous mixture; R stands for the gas constant; and concentration is given as the mole/volume ratio $C = N_\Omega/V$. Isobaric operation in the liquid phase is assumed to be given as

$$P_l = P_{l,\text{in}}, \tag{4b}$$

where $P_{l,\text{in}}$ corresponds to the pressure in the liquid inflow. Neglecting mixing effects, the relation between the energy holdup and the temperature for each phase corresponds to

$$U_l = \sum_{j=1}^{c} N_{l,j}\bar{U}_{l,o,j} + N_{l,j}\bar{\mathcal{C}}_{v,g,j}(T_g - T_{l,o}) \tag{5a}$$

$$U_g = \sum_{j=1}^{c} N_{g,j}\bar{U}_{g,o,j} + N_{g,j}\bar{\mathcal{C}}_{v,l,j}(T_l - T_{g,o}), \tag{5b}$$

where $\bar{U}_o$ represents a partial molar internal energy reference state at temperature T_o; and $\bar{\mathcal{C}}_{v,j}$ stands for the molar heat capacity for component j. Flow velocity is considered as a state function of the flow velocity v, which in turn depends on the kinetic energy of the phase

$$F_{l,V} = A_{l,\text{out}}v_l, \qquad v_l = \sqrt{2K_l/M_l} \tag{6a}$$

$$F_{g,V} = A_{g,\text{out}}v_g, \qquad v_g = \sqrt{2K_g/M_g} \tag{6b}$$

where A_{out} stands for outflow cross sectional area, and $M = \sum_1^c \bar{M}_j N_j$ represents mass holdup in the bulk-phase.

Equations (3)-(6) stand as the constitutive equations for the model (1)-(2). In the next section, the model description is completed by describing the interface transport rates $(n_{l,j}, e_{l,u}, e_{l,k}, n_{g,j}, e_{g,u}, e_{g,k})$ as function of irreversible processes occurring around the interface.

2.2 Interface transport rates

Two boundary layers are assumed to surround the gas-liquid interface, as depicted in Figure 3. The interface between the layers is assumed to be locally at thermodynamic equilibrium with composition $(x_{i,1}, y_{i,1}, \ldots, x_{i,c}, y_{i,c})$ temperature T_i, and pressure P_i. The interfacial values are given as the solution to a boundary value problem, where the boundary conditions are set by the bulk-phases (Taylor and Krishna, 2000).

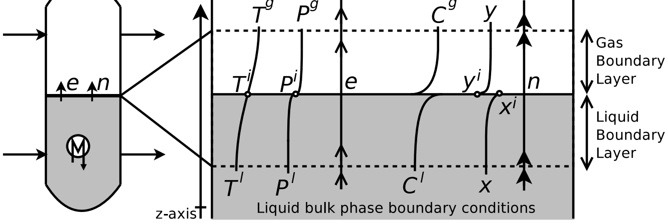

Fig. 3. Interface in a liquid-vapor System

Inhomogeneities between both bulk-phases are the driving forces between mass and energy flows across the interface. Molar transport is the addition of diffusive and convective transport processes (Taylor and Krishna, 2000). Neglecting multicomponent coupled diffusion we can write

$$n_{l,j} = k_{l,j}C_l(x_j - x_{i,j}) + x_j n_\Omega, \quad j = 1, \ldots, c-1 \tag{7a}$$

$$n_{g,j} = k_{g,j}C_g(y_{i,j} - y_j) + y_j n_\Omega, \quad j = 1, \ldots, c-1, \tag{7b}$$

where $k_{l,j}$ and $k_{g,j}$ stand for mass transport coefficients in liquid and gas boundary layers, respectively; and $n_\Omega := \sum n_{l,j} = \sum n_{g,j}$ corresponds to the total molar flow across the interface.

The total energy flowing across the interface is the sum of thermal, convective, and kinetic energy transport phenomena (Bird et al., 2002)

$$e_l = h_{l,i}(T_l - T_i) + \sum_{j=1}^{c} \bar{H}_{l,j}n_{l,j} + \tfrac{1}{2}v_{l,i}^2 m_\Omega \tag{8}$$

$$e_g = h_{g,i}(T_i - T_g) + \sum_{j=1}^{c} \bar{H}_{g,j}n_{g,j} + \tfrac{1}{2}v_{g,i}^2 m_\Omega, \tag{9}$$

where $h_{l,i}$ and $h_{g,i}$ represent conductive transport coefficients; $\bar{H}_j$ stands for the partial molar entropy of component j; $m_\Omega := \sum \bar{M}_j n_{l,j} = \sum \bar{M}_j n_{g,j}$ corresponds to the total mass flowing through a boundary layer; and,

$$v_{l,i} = m_\Omega/(A_i\rho_l), \qquad v_{g,i} = m_\Omega/(A_i\rho_g),$$

represent the average velocity of the flow crossing the boundary layers (not to be confused with the bulk-phase convective outflow velocities v_l and v_g). In the previous equation, A_i stands for the interface area, and ρ for the density.

The mechanical energy of a fluid flow accounts for three energy components: kinetic energy, potential energy, and PV work. Since potential energy variations are neglected, mechanical energy flowing across the interface is written as

$$e_{l,K} = \tfrac{1}{2}v_{l,i}^2 m_\Omega + P_l\tilde{V}_l m_\Omega \tag{10a}$$

$$e_{g,K} = \tfrac{1}{2}v_{g,i}^2 m_\Omega + P_g\tilde{V}_g m_\Omega, \tag{10b}$$

where $\tilde{V} = 1/\rho$ stands for the volume per unit of mass of the flow. The internal energy flow-rate corresponds to what remains when subtracting the mechanical energy flow from total energy being transported through the interface,

$$e_U := e - e_K.$$

Neglecting enthalpy diffusive transport, the internal energy flows correspond to

$$e_{l,U} = h_{l,i}(T_l - T_i) + \sum_{j=1}^{c} \bar{U}_{l,j}n_{l,j} \tag{11a}$$

$$e_{g,U} = h_{g,i}(T_i - T_g) + \sum_{j=1}^{c} \bar{U}_{g,j}n_{g,j} \tag{11b}$$

Careful inspection of equations (7)–(11) reveals that we can write the interface transport rates as functions of $2c+3$ interface variables

$$(y_{i,1}, x_{i,1}, \ldots, x_{i,c}, y_{i,c}, T_i, P_i, n_\Omega), \tag{12a}$$

together with interface boundary conditions

$$(T_g, T_l, P_g, P_l, C_g, C_l, x_1, \ldots, x_{c-1}, y_1, \ldots, y_{c-1}), \tag{12b}$$

given by the bulk-phases. In the next section, the interface is described as a nonlinear algebraic system.

2.3 Interface algebraic system

The interface for a non-homogeneous stationary system was first presented by Krishnamurthy and Taylor (1985). Their study relies on describing interfacial temperature T_i, pressure P_i, and compositions (x_j, y_j) using two fundamental assumptions:

(iv) Neither mass nor energy accumulate in the boundary layers surrounding the interface, nor in the interface itself; and,
(v) The interface, seen as the contact surface between both boundary layers, is locally at thermodynamic equilibrium.

Equality in molar flow rates (7)

$$k_{g,j}C_g(y_{i,j}-y_j)+y_jn_\Omega = k_{l,j}C_l(x_j-x_{i,j})-x_jn_\Omega \qquad j=1,\dots,c-1, \tag{13}$$

and equality in energy flow rates (8)

$$\begin{aligned} &h_{g,i}(T_i-T_g)+\textstyle\sum_{j=1}^{c}\bar{H}_{g,j}n_{g,j}+\frac{1}{2}v_{g,i}^2m_\Omega \\ &\quad = h_{l,i}(T_l-T_i)+\textstyle\sum_{j=1}^{c}\bar{H}_{l,j}n_{l,j}+\frac{1}{2}v_{l,i}^2m_\Omega, \end{aligned} \tag{14}$$

follow from assumption (iv). Local equilibrium, assumption (v), requires that

$$y_{i,j} = K_j(T_i,P_i,x_{i,1},\dots,x_{i,c})x_{i,j}, \quad j=1,\dots,c \tag{15a}$$

$$1 = \textstyle\sum_{j=1}^{c}x_{i,j} \tag{15b}$$

$$1 = \textstyle\sum_{j=1}^{c}y_{i,j}, \tag{15c}$$

where $K_j(\cdot)$ represents the nonlinear liquid-vapor composition ratio. To complete the system description, we balance the mechanical energy around each boundary layer surrounding the interface. Assuming that the fluid velocity is approximately the same close to the interface, we write

$$\frac{P_l-P_i}{\rho_l}-\frac{P_g-P_i}{\rho_g}=\frac{1}{2}\left(v_{g,i}^2-v_{l,i}^2\right). \tag{16}$$

Equations (13)–(16) sum to $2c+3$ equations, that depend on $2c+3$ interface variables (12a), and on $2c+4$ intensive variables (12b) that depend on the state of each bulk-phase. In the next section, the bulk-phase description is put together with the algebraic system defining the flash-drum DAE system.

2.4 Flash-drum differential algebraic system

Interface transport equations (13)–(16) are written in terms of intensive variables. To match the interface and bulk-phase descriptions, the bulk-phase dynamics (1)–(6) is rewritten as differential equations of the intensive variables:

(a) Temperature variations

$$\begin{aligned}\mathcal{C}_{v,g}\dot{T}_g &= F_{g,V,in}(T_{g,in}-T_g)\bar{\mathcal{C}}_{v,g,in} \\ &\quad + h_{g,\infty}(T_{g,\infty}-T_g)+h_{g,i}(T_i-T_g)\end{aligned} \tag{17a}$$

$$\begin{aligned}\mathcal{C}_{v,l}\dot{T}_l &= F_{l,V,in}(T_{l,in}-T_l)\bar{\mathcal{C}}_{v,l,in} \\ &\quad + h_{l,\infty}(T_{l,\infty}-T_l)-h_{l,i}(T_l-T_i)\end{aligned} \tag{17b}$$

where $\bar{\mathcal{C}}_v = \sum_{j=1}^{c}C_j\bar{\mathcal{C}}_{v,j}$ and $\mathcal{C}_v = V\sum_{j=1}^{c}C_j\bar{\mathcal{C}}_{v,j}$ represent molar and total heat capacities respectively, and h_∞ is the thermal conductivity constant for a heat exchanger at temperature T_∞.

(b) Composition variations

$$\begin{aligned}C_gV_g\dot{y}_j &= F_{g,V,in}C_{g,in}\left(y_{j,in}-y_j\right) \\ &\quad + k_{g,j}C_g(y_{i,j}-y_j), \quad j=1,\dots,c-1\end{aligned} \tag{18a}$$

$$\begin{aligned}C_lV_l\dot{x}_j &= F_{l,V,in}C_{l,in}\left(x_{j,in}-x_j\right) \\ &\quad - k_{l,j}C_l(x_j-x_{i,j}), \quad j=1,\dots,c-1\end{aligned} \tag{18b}$$

(c) Concentration variations

$$\begin{aligned}V_g\dot{C}_g &= F_{g,V,in}C_{g,in} \\ &\quad - C_g\left(F_{g,V}+\dot{V}_g\right)+n_\Omega\end{aligned} \tag{19a}$$

$$V_l\dot{C}_l = F_{l,V,in}C_{l,in}-C_l\left(F_{l,V}+\dot{V}_l\right)-n_\Omega \tag{19b}$$

(d) PV work variations

$$\dot{P}^g = ZR(T_g\dot{C}_g+C_g\dot{T}_g) \tag{20a}$$

$$\dot{P}_l = \dot{P}_{in}^l \tag{20b}$$

$$\dot{V}_g = -\dot{V}_l \tag{20c}$$

$$\begin{aligned}\dot{V}_l &= \textstyle\sum_{j=1}^{c}\bar{V}_{l,j}\big(x_{j,in}F_{l,V,in}C_{l,in} \\ &\quad - x_jF_{l,V}C_l-k_{l,j}C_l(x_j-x_{i,j})-x_jn_\Omega\big)\end{aligned} \tag{20d}$$

(e) Volumetric outflow variations

$$\begin{aligned}\tfrac{v_lM_l}{A_{l,out}}\dot{F}_{l,V} &= \left(\tfrac{1}{2}\left(v_{g,in}^2-v_g^2\right)\rho_{g,in}+P_{g,in}\right)F_{g,V,in} \\ &\quad - P(F_{g,V}+\dot{V}_g)+\left(\tfrac{1}{2}(v_{i,g}^2-v_g^2)+\tfrac{P_g}{\rho_g}\right)m_\Omega\end{aligned} \tag{21a}$$

$$\begin{aligned}\tfrac{v_gM_g}{A_{l,out}}\dot{F}_{g,V} &= (\tfrac{1}{2}(v_{l,in}^2-v_l^2)\rho_{l,in}+P_{l,in})F_{l,V,in} \\ &\quad - P\left(F_{l,V}+\dot{V}_l\right)-\left(\tfrac{1}{2}(v_{i,l}^2-v_l^2)+\tfrac{P_l}{\rho_l}\right)m_\Omega\end{aligned} \tag{21b}$$

where $M = V\sum\bar{M}_jC_j$ represents the total mass holdup in the flowing bulk phase.

The interface algebraic system remains as

$$\begin{aligned}0 &= k_{g,j}C_g(y_{i,j}-y_j)-k_{l,j}C_l(x_j-x_{i,j})+(y_j-x_j)n_\Omega, \\ &\qquad j=1,\dots,c-1.\end{aligned} \tag{22a}$$

$$\begin{aligned}0 &= h_{g,i}(T_i-T_g)-h_{l,i}(T_l-T_i) \\ &\quad + \textstyle\sum_{j=1}^{c}\Delta\bar{H}_jn_j+\frac{1}{2}(v_{g,i}^2-v_{l,i}^2)m_\Omega\end{aligned} \tag{22b}$$

$$0 = \frac{1}{2}(v_{g,i}^2-v_{l,i}^2)-\frac{P_l-P_i}{\rho_l}+\frac{P_g-P_i}{\rho_g} \tag{22c}$$

$$\begin{aligned}0 &= y_{i,j}-K_j(T_i,P_i,x_{i,1},\dots,x_{i,c})x_{i,j}, \\ &\qquad j=1,\dots,c.\end{aligned} \tag{22d}$$

$$0 = 1-\textstyle\sum_{j=1}^{c}x_j^i \tag{22e}$$

$$0 = 1-\textstyle\sum_{j=1}^{c}y_j^i, \tag{22f}$$

where $\Delta\bar{H}_j = \bar{H}_{g,j}-\bar{H}_{l,j}$ corresponds to the partial enthalpy of vaporization of component j, and $n_j := n_{l,j} = n_{g,j}$.

3. LYAPUNOV FIRST METHOD FOR DAE SYSTEMS

The complete flash drum dynamic model equations (17)–(22) is a semi-explicit DAE system of the form

$$\dot{z} = f(z,w,u) \tag{23a}$$

$$0 = g(z,w), \tag{23b}$$

where

$$\begin{aligned}z = (&T_g,T_l,P_l,P_g,x_1,y_1,\dots,x_{c-1},y_{c-1}, \\ &C_l,C_g,V_l,V_g,F_{l,V},F_{g,V})\end{aligned} \tag{24a}$$

refers to bulk-phase intensive variables,

$$w = (T_i,P_i,x_{i,1},y_{i,1},\dots,x_{i,c},y_{i,c},n_\Omega) \tag{24b}$$

denotes the interface variables, and the vector

$$\begin{aligned}u = (&T_{g,in},T_{l,in},T_{g,\infty},T_{g,\infty},P_{l,in},P_{g,in},F_{l,V,in}, \\ &F_{g,V,in},x_{1,in},y_{1,in},\dots,x_{c-1,in},y_{c-1,in})\end{aligned} \tag{24c}$$

stands for input variables set by the environment surrounding the system.

We briefly review stability theory for linear DAE systems, following the Lyapunov first method. A complete exposition on Lyapunov stability for DAE systems can be found in Yang et al. (2013). The input vector u is assumed to be fixed as $u^\star$. Let $(z^\star, w^\star)$ be an isolated equilibrium point of (23), *i.e.*,

$$\begin{aligned} 0 &= f_u(z^\star, w^\star) \\ 0 &= g(z^\star, w^\star), \end{aligned}$$

where $f_u = f(z^\star, w^\star, u^\star)$. From Brenan et al. (1996), we know that the semi-explicit DAE (23) is of index one if and only if the Jacobian $\partial g/\partial z$ is non-singular. For DAE systems of index one, the z dynamics linearized around $(z^\star, w^\star)$ can be written as

$$\dot{z} = \left[\frac{\partial f_u}{\partial z} - \frac{\partial f_u}{\partial w} \frac{\partial g}{\partial w}^{-1} \frac{\partial g}{\partial z} \right] \bigg|_{(z^\star, w^\star)} (z - z^\star), \qquad (25)$$

where the partial derivatives stand for Jacobian matrices. Lyapunov's first method states that if the spectrum of the linearized system (25) is contained in the left half-complex plane, then the equilibrium point $(z^\star, w^\star)$ is locally stable (Yang et al., 2013). We illustrate this with an example in the following Section.

4. EXAMPLE AND NUMERICAL SIMULATIONS

A non-ideal methanol-water mixture is considered to illustrate the proposed model and its analysis. With two components, the DAE system (23) is given by 19 equations and 19 variables. Fixing the inputs to be at thermodynamic equilibrium $(T^\star, P^\star, x^\star, y^\star)$, the stationary state corresponds to

$$\begin{aligned} z^\star &= (T^\star, T^\star, P^\star, P^\star, x_1^\star, y_1^\star, C_l^\star, C_g^\star, V_l^\star, V_g^\star, F_V^\star, F_V^\star) \\ w^\star &= (T^\star, P^\star, x_1^\star, y_1^\star, x_2^\star, y_2^\star, 0), \end{aligned}$$

where $C^\star$ is determined from (3a) and (4a). Interface temperature and liquid vapor equilibrium are set using Antoine and Margules thermodynamic models for equilibrium (Sandler, 1999).

To determine the steady state, the inflow properties are assumed at thermodynamic equilibrium at 351.24 K (78.09^oC) and 101.3 kPa (0.9998 atm); inflows are fixed at 1 m^3/s; and the liquid phase is set to occupy 10% of the total volume $V_T = 1\ m^3$. At these conditions, the stationary state $(z^\star, w^\star)$ has values given in Table 1.

Table 1. Stationary State

$T^\star = 78.09\ ^oC$,	$x_1^\star = 0.2764$,	$V_l^\star = 0.1\ m^3$
$P^\star = 101.3\ kPa$,	$y_1^\star = 0.6615$,	$F_V^\star = 1\ m^3/s$

The Jacobian $(\partial g/\partial w)$ is full rank at the stationary state, making the DAE system of index one locally around the equilibrium for the methanol-water mixture. Next, we assess stability for two operation regimes.

4.1 Stability analysis for two operation regimes

Scenario 1 (non-isobaric operation regime). At equilibrium, the linearized system (25) has rank 10. The rank deficiency follows as a consequence from the constant inflow pressure (equation (20b) is null) and the symmetry between the volume dynamics (20c) and (20d). The equilibrium is not stable as the spectrum of the linearized system contains one positive eigenvalue $\lambda_1 \approx 6.55 \times 10^{-6}$. Besides the two zero eigenvalues, the rest of the spectrum is contained in the left half real line, between $\lambda_2 \approx -3.45 \times 10^{-8}$ and $\lambda_{10} \approx -1.2 \times 10^5$.

Scenario 2 (isobaric operation regime). We include a perfect pressure controller in the descriptor system, making $P_l = P_g = P^\star$. Under this assumption, the spectrum of the linearized system contains three zeros and a two pair of positive complex conjugate eigenvalues close to the real axis $\lambda_{1,2} \approx -1.65 \times 10^{-7}(10^{-4} \pm j)$. The remaining eigenvalues are negative and go from $\lambda_3 \approx -1$ to $\lambda_9 \approx -1.2 \times 10^5$.

4.2 Numerical simulations for isobaric operation

We present two dynamic simulations for the stable Scenario 2. The system is disturbed from stationary state by an increase in the inflow temperature. In the first case, the inflow temperature returns to its original value and the system returns to its initial equilibrium; in the second case, maintaining the inflow temperature at its higher value leads to complete evaporation of the liquid phase.

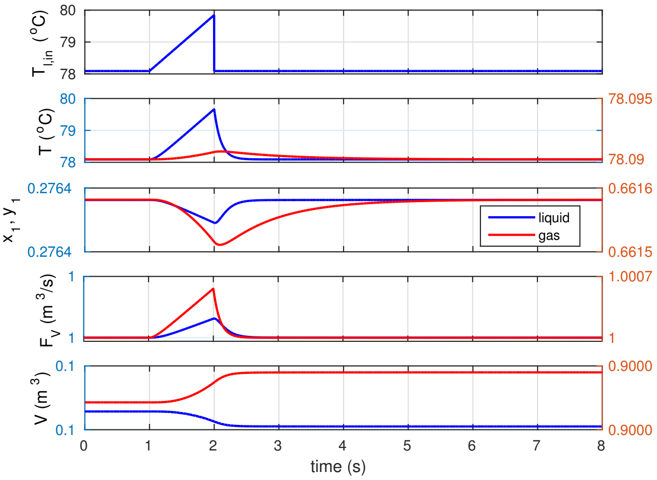

Fig. 4. Numerical simulation 1, liquid phase trajectories (blue) are referred to the left y-axis; gas phase trajectories (red) to the right y-axis. Time is presented in logarithmic scale.

Numerical simulation 1 (Figure 4). A ramp disturbance is introduced in the liquid inflow temperature for $1 \leq t < 2$. The system reacts to the disturbance and inhomogeneities in temperature and composition appear between both phases. As a consequence of the inhomogeneities, transfer processes redistribute the mass and the energy in the system. The mass redistribution causes the volume of each phase to change. At $t = 2$, the inflow temperature goes back its nominal value $T_{l,in} = T^\star$. After the disturbance is removed, the equilibrium state is recovered.

Numerical simulation 2 (Figure 5). A step disturbance in the inflow liquid temperature is introduced. In contrast with Scenario 1, the liquid inflow temperature remains disturbed at $T_{l,in} = 1.05 \times T^\star$ for $t \geq 2$. This causes the system to remain far from thermodynamic equilibrium. As a consequence, transport processes between phases do

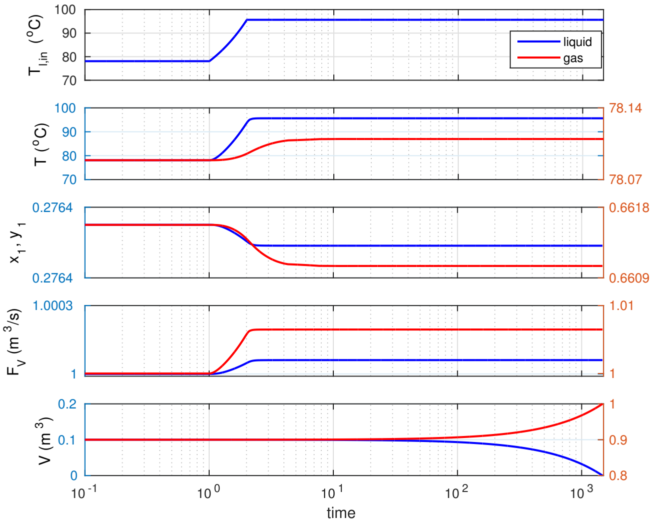

Fig. 5. Numerical simulation 2, liquid phase trajectories (blue) are referred to the left y-axis; gas phase trajectories (red) to the right y-axis.

not vanish and the liquid phase evaporates completely around $t \approx 1,470s$. For better appreciation of the dynamic behavior, Figure (5) is presented using a log scale for time.

5. CONCLUSIONS

In this article, modeling aspects of dynamic flash-drum systems were explored using a non-equilibrium physics-based model. The description presented considers transport phenomena formulations and conservation principles and leads to a nonlinear DAE system. The proposed dynamic model describes the evolution of liquid and vapor phases as separated sub-systems interconnected through an interface. The introduction of the interface exchange rates in the model predicts phase collapse for systems that operate consistently far from equilibrium. Moreover, the model presented can be easily extended to describe liquid-liquid or liquid-solid multiphase systems far from equilibrium. The obtained DAE system is shown to be of index one for a methanol-water mixture. Numerical evidence shows that the linearized system has positive eigenvalues for a non-isobaric operation regime. For the isobaric case, trajectories appear stable in simulations; however, numerical error in the linearization eigenvalues would lead us to conclude otherwise. Developing a complete nonlinear stability analysis approach for the DAE model developed here is therefore required and will be addressed in future research. A thermodynamic-based dissipativity approach, following (Willems, 1972; Alonso and Ydstie, 1996) will be considered to get an input-output perspective on the problem of multiphase chemical systems.

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