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Numerical evaluation of the stability of stationary points of index-2 differential-algebraic equations: Applications to reactive flash and reactive distillation systems

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ABSTRACT

The dynamic behavior of many chemical processes can be represented by an index-2 system of differential-algebraic equations. This index can be reduced by differentiation, but unfortunately the index reduced systems are not guaranteed to possess the same stability characteristics as that of the original system. When the set of differential-algebraic equations can be written in Hessenberg form, the matrix pencil of the linearized system can be used to directly evaluate the stability of a steady state without the need for index reduction. Direct evaluations of stability of reactive flash and reactive distillation are presented. It is also shown that a commonly used index reduction will always result in null eigenvalues at steady state. Stabilization methods were successfully applied to this reduced system. An alternative index reduction method for a reactive flash is generalized and shown to be highly sensitive to minor changes in the jacobian.

1. Introduction

Consider the autonomous system of differential-algebraic equations

$$A\frac{d\boldsymbol{x}}{dt}=\boldsymbol{f}(\boldsymbol{x}) \tag{1}$$

If the constant coefficient matrix A is non-singular, Eq. (1) represents a system of ordinary-differential equations (ODE). In cases where matrix A is not of full-rank, the system is a differential-algebraic equation (DAE).

It is well known (e.g. Froment, Bischoff, & De Wilde, 2010) that a continuous stirred tank reactor (CSTR) with a single liquid phase has a dynamic representation in the form of Eq. (1) with a coefficient matrix of full-rank. Therefore the stability of a steady state can be analytically determined by checking the eigenvalues of the jacobian matrix, $\partial\boldsymbol{f}/\partial\boldsymbol{x}$. In the event that all eigenvalues have negative real parts, that steady state is stable and small dynamic perturbations will return to the state. When the CSTR model is extended to include mass transfer between the liquid and vapor phases, a reactive flash results. If the rate of this mass transfer is assumed to be very fast in comparison to other time constants of the reactive flash, then the dynamic representation is a DAE. The algebraic constraints in this case are the vapor–liquid equilibrium equations. Tracing the orbit of such a system and determining the stability of its steady states can be considerably more difficult than is the case with ODE's.

A critical property of a DAE system is the index. There are a number of definitions for this integer-valued parameter, but the most straightforward is the differentiation index, which is defined as the number of times that all or part of the system must be differentiated with respect to time in order to reduce the system to its underlying ODE (Brenan, Campbell, & Petzold, 1996).

For example, many chemical engineering systems can be written in the semi-explicit form

$$\boldsymbol{x}'=\boldsymbol{f}(\boldsymbol{x})+\boldsymbol{b}(\boldsymbol{x})\boldsymbol{y} \tag{2a}$$

$$0=\boldsymbol{g}(\boldsymbol{x}) \tag{2b}$$

Successive differentiation of the algebraic constraint (2b) results in

$$0=\frac{\partial\boldsymbol{g}}{\partial\boldsymbol{x}}(\boldsymbol{f}(\boldsymbol{x})+\boldsymbol{b}(\boldsymbol{x})\boldsymbol{y}) \tag{2c}$$

$$0=\left(\left(\frac{\partial\boldsymbol{g}}{\partial\boldsymbol{x}}\boldsymbol{f}(\boldsymbol{x})\right)_{\boldsymbol{x}}+\left(\frac{\partial\boldsymbol{g}}{\partial\boldsymbol{x}}\boldsymbol{b}(\boldsymbol{x})\right)_{\boldsymbol{x}}\boldsymbol{y}\right)(\boldsymbol{f}(\boldsymbol{x})+\boldsymbol{b}(\boldsymbol{x})\boldsymbol{y})+\left(\frac{\partial\boldsymbol{g}}{\partial\boldsymbol{x}}\boldsymbol{b}(\boldsymbol{x})\right)\boldsymbol{y}' \tag{2d}$$

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Nomenclature

F	liquid feed rate (mol/min)
H	liquid molar holdup (mol)
h_{feed}	specific enthalpy of feed stream (J/mol)
h_{liq}	specific enthalpy of liquid exit (J/mol)
h_{vap}	specific enthalpy of vapor exit (J/mol)
K_i	ratio of vapor to liquid mole fraction of component i
L	liquid exit flow (mol/min)
l	specific liquid molar exit rate (=L/F)
p_i^{SAT}	vapor pressure of component i (Pa)
r_j	rate of reaction j (min^{-1})
q	External heat input to flash, Q divided by feed rate F (J/mol)
T	temperature (K)
V	vapor exit flow (mol/s)
x_i	liquid mole fraction of component i
z_i	feed mole fraction of component i
Greek	
$\nu_{i,j}$	stoichiometric coefficient of component i in reaction j
$\nu_{T,j}$	sum of stoichiometric coefficients in reaction j
τ	reactive flash time constant (=H/F) (min)
ϕ	vapor fraction (=V/F)

Rearranging (2d) allows an expression for $d\boldsymbol{y}/dt$ to be generated, and the combination of (2a) and (2d) represents the underlying ODE of the original DAE, whose differentiation index is two.

It should be noted that when the DAE is in the form of Eqs. (2a) and (2b) and the matrix ($\partial\boldsymbol{g}/\partial\boldsymbol{x}\,\boldsymbol{b}(x)$) is non-singular, the index-2 system can be converted to an ODE after only one differentiation by rewriting (2c) to get an expression for $\boldsymbol{y}$ and then substituting into (2a) to obtain

$$\boldsymbol{x}' = \boldsymbol{f}(\boldsymbol{x}) - \boldsymbol{b}(\boldsymbol{x})\left(\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}\boldsymbol{b}(\boldsymbol{x})\right)^{-1}\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}\boldsymbol{f}(\boldsymbol{x}) \tag{3}$$

Numerical solutions of higher index DAEs (differentiation index of 2 or higher) can be obtained from the underlying ODE via index reductions of this type. An obvious difficulty that arises is that constants of integration are introduced every time the algebraic constraint is differentiated. Potential pitfalls and implementation aspects are discussed in detail by Brenan et al. (1996), Gear (1988) and Ascher and Petzold (1998).

Kumar and Daoutidis (1995) developed a generalized index reduction algorithm, which exploited the equation form (2a) and (2b), and used this algorithm to create a state-space realization of a reactive flash. In a somewhat similar manner, Rahul, Pavan Kumar, Dwivedi, and Kaistha (2009) reduced the index of a reactive distillation system by differentiating the algebraic constraint and using the resultant equation to derive an expression for the molar vapor flow on each stage of the column.

A dynamic model of an ethylene glycol reactive-distillation column with non-zero vapor holdup was developed by Kumar and Daoutidis (1999). The stability of steady states of this system were not evaluated directly, but were extracted instead from the underlying index-1 model that did not include vapor holdup. This stability prediction was justified based on the fact that the dynamic and underlying models had identical solutions at steady state. A different method to determine steady state stability of a reactive distillation was used by Chen, Huss, Doherty, and Malone (2002), who labeled a solution as stable if the Backward Differentiation Formula of Gear (1971) converged to it from a reasonable starting point. They indirectly reduced the index of the system by solving for the liquid and vapor stage flows independently. Rodriguez, Zheng, and Malone (2001) applied an alternative index reduction to evaluate the stability of the steady states of a reactive flash.

In cases where multiple solutions occur in a reactive flash, the bifurcation curve quite often assumes an ‘S’ shape. A number of authors (Luyben, 1993; Monroy-Loperena & Alvarez-Ramirez, 1999) have extended the results familiar from the study of a single phase CSTR and postulated that the middle solutions on the reversed portion of the ‘S’ are unstable. The results presented in this paper do not contradict this assumption, but do provide methods for analytically determining the stability of a solution without necessarily having to traverse the bifurcation path of steady states, and therefore is independent of any knowledge of solution multiplicity.

2. Direct calculation of stability

2.1. Theory

März (1994, 1998) presented two important theorems on the stability of index-1 and index-2 DAE’s in the general form of Eq. (1) that are repeated here.

Theorem 1. *$\boldsymbol{f}(\boldsymbol{x}) \in C^2$ on an open bounded region D, containing a stationary point $\boldsymbol{x}^*$, $\boldsymbol{f}(\boldsymbol{x}^*) = 0$. Let the matrix pencil ($\lambda A - B$) be regular with index 1 and all its generalized eigenvalues have negative real parts. Then the DAE is Lyapunov stable at this stationary point.*

Theorem 2. *$\boldsymbol{f}(\boldsymbol{x}) \in C^2$ on an open bounded region D, containing a stationary point $\boldsymbol{x}^*$, $\boldsymbol{f}(\boldsymbol{x}^*) = 0$. Let the matrix pencil ($\lambda A - B$) be regular with index 2 and all its generalized eigenvalues have negative real parts. Additionally, let the DAE be in Hessenberg form of size 2. Then the DAE is Lyapunov stable at this stationary point.*

The matrix B is simply the jacobian matrix $\partial\boldsymbol{f}/\partial\boldsymbol{x}$ of Eq. (1) evaluated at the stationary point $\boldsymbol{x}^*$. While defined very differently, the index of the matrix pencil has the same value as the differentiation index defined earlier when the DAE can be written in Hessenberg form. Regularity of the matrix pencil requires simply that there exist values of λ such that the matrix pencil ($\lambda A - B$) is non-singular.

An autonomous DAE is in ‘Hessenberg’ form of size 2 if it can be written in the following form (Brenan et al., 1996)

$$\boldsymbol{x}' = \boldsymbol{f}(\boldsymbol{x}, \boldsymbol{y}) \tag{4}$$

$$0 = \boldsymbol{g}(\boldsymbol{x}) \tag{5}$$

with $(\partial\boldsymbol{g}/\partial\boldsymbol{x})(\partial\boldsymbol{f}/\partial\boldsymbol{y})$ being non-singular. The dynamic representation of a reactive flash (and many other chemical engineering processes) can be written in this form. It should be noted that the second theorem of März (1994) can be generalized beyond Hessenberg form DAE’s under certain conditions, but this topic is beyond the scope of this paper.

The theorems of März (1994, 1998) provide necessary conditions for stability but do not state if they are sufficient. This appears to be a more subtle issue, but Riaza (2010) has addressed the question in the context of general quasilinear DAEs and stated that when traversing a bifurcation path of steady states, a transition of the real part of an eigenvalue from $\mathbb{R}^-$ to $\mathbb{R}^+$ does indeed correspond to a loss of stability of the steady state if the remaining eigenvalues remain on $\mathbb{C}^-$.

2.2. Reactive flash example

The dynamic representation of a P–Q reactive flash with r reactions, n components, constant molar holdup H, liquid molar feed rate F and ideal vapor–liquid equilibrium can be written as follows;

$$\tau\frac{dx_i}{dt} = z_i - x_i - \phi(K_i x_i - x_i) - \tau\left(x_i\sum_{j=1}^{r}\nu_{T,j}r_j - \sum_{j=1}^{r}\nu_{i,j}r_j\right), \quad i = 1, \ldots, n-1 \tag{6}$$

$$\tau C_p\frac{dT}{dt} = h_{feed} + q - h_{liq} - h_{liq}\tau\sum_{j=1}^{r}\nu_{T,j}r_j + \phi(h_{liq} - h_{vap}) \tag{7}$$

$$K_n\left(1 - \sum_{i=1}^{n-1}x_i\right) + \sum_{i=1}^{n-1}K_i x_i - 1 = 0 \tag{8}$$

noting that the constant molar holdup requires that

$$0 = 1 - l - \phi + \tau\sum_{j=1}^{r}\nu_{T,j}r_j \tag{9}$$

The particular case considered here will be an adaption of the ethylene glycol reactive flash presented by Rodriguez, Zheng, and Malone (2004), with the primary reaction of ethylene oxide and water to produce ethylene glycol and a competing reaction of ethylene glycol with ethylene oxide, both of which are considered irreversible.

$$\begin{aligned} &C_2H_4O + H_2O \xrightarrow{r_1} C_2H_6O_2 \\ &C_2H_4O + C_2H_6O_2 \xrightarrow{r_2} C_4H_{10}O_3 \end{aligned} \tag{10}$$

With ethylene oxide, water, ethylene glycol and diethylene glycol labeled as components *A*, *B*, *C* and *D*, respectively, the reaction rate and vapor pressure equations are given by;

$$r_1 = 3.2023 \times 10^9 \exp\left(-\frac{9360.845}{T}\right) x_A x_B \tag{11}$$

$$r_2 = 5.84 \times 10^9 \exp\left(-\frac{9360.845}{T}\right) x_A x_C \tag{12}$$

$$p_A^{SAT} = \exp\left(21.3066 - \frac{2428.2}{T - 35.388}\right) \tag{13}$$

$$p_B^{SAT} = \exp\left(23.2256 - \frac{3835.18}{T - 45.34}\right) \tag{14}$$

$$p_C^{SAT} = \exp\left(25.1431 - \frac{6022.18}{T - 28.25}\right) \tag{15}$$

$$p_D^{SAT} = \exp\left(23.8578 - \frac{6085.25}{T - 26.15}\right) \tag{16}$$

Liquid and vapor specific enthalpies are determined using the latent heat models of Eqs. (17) and (18), neglecting the sensible heat of the vapor phase.

$$h_{liq} = \sum_{i=1}^{n}(\Delta_f H^0_{liq,i} + Cp_i(T - 298))x_i \tag{17}$$

$$h_{vap} = \sum_{i=1}^{n}(\Delta_f H^0_{liq,i} + Cp_i(T_{boil} - 298) + \Delta H_{vap,i})y_i \tag{18}$$

Component specific data are shown in Table 1. Heat of formation and heat capacity data were obtained from the NIST Chemistry WebBook (Afeefy, Liebman, & Stein, 2012). The heat of formation data used predicts a heat of reaction at standard conditions of −78.47 kJ/mol for the primary reaction and −72.8 kJ/mol for the secondary reaction. The pressure is atmospheric, feed temperature is 298 K and the specific heat (addition), *q*, is set at 2.282 kJ/mol of feed.

Table 1
Component specific data for Reactive Flash Problem.

	EO	H_2O	EG	DEG
C_p (kJ/mol K)	0.0869	0.0754	0.1498	0.2870
$\Delta_f H^\circ{}_{liq}$ (kJ/mol)	−95.7	−285.83	−460	−628.5
ΔH_{vap} (kJ/mol)	25.543	40.6603	53.186	56.944
z	0.5	0.5	0	0

It is straightforward to show that Eqs. (6)–(8) are in the Hessenberg form defined by Eqs. (4) and (5) when the variables are $\boldsymbol{x} = [x_1, x_2, x_3, T]$ and $\boldsymbol{y} = [\phi]$, and therefore that the theorem of März applies for this index-2 DAE system. The requirement that $(\partial \boldsymbol{g}/\partial \boldsymbol{x})(\partial \boldsymbol{f}/\partial \boldsymbol{y})$ be non-singular is equivalent in this case to stating that the vapor fraction ϕ be finite.

A steady state solution was determined and using the system time constant $\tau = H/F$ as a continuation parameter, the path of steady state solutions was tracked using PITCON (Rheinboldt & Burkardt, 1983) and the generalized eigenvalues of the matrix pencil were calculated using LAPACK routines (Anderson et al., 1999). For the energy balance, the overall heat capacity used in the eigenvalue calculations was defined as simply the molar average at that particular steady state. Fig. 1 shows the continuation path for the vapor fraction ϕ and steady state stability properties evaluated at large values of the time constant where a region of steady state multiplicity exists. The generalized eigenvalue with maximum real part changed sign at the turning points and was positive in the middle section, indicating a transition to unstable steady states. As with ODE's, the ordering of the equations and variables should correspond, which in the case of steady state simulators, may require a re-ordering of the equations or variables.

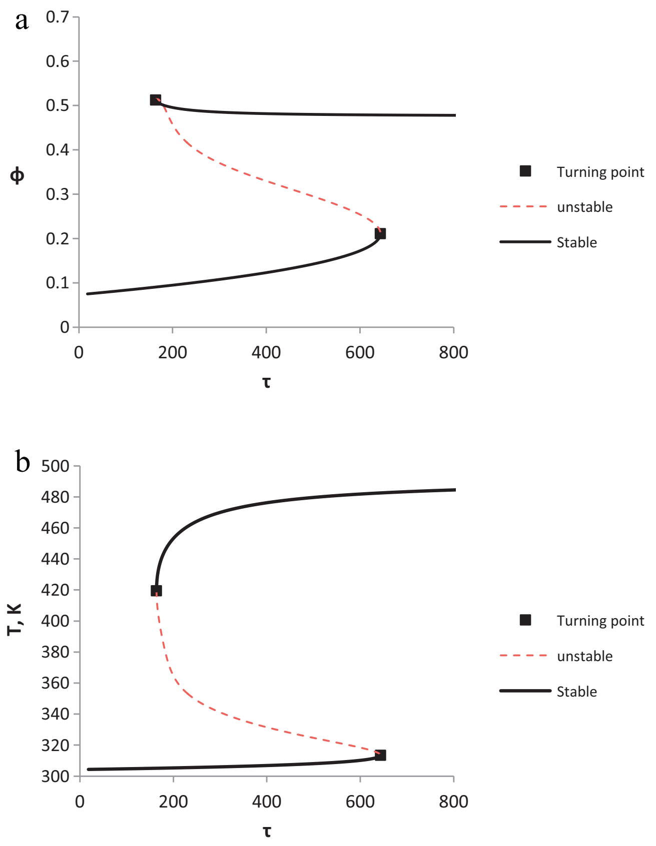

Fig. 1. (a and b) Steady state vapor fraction for the reactive flash example. Stability determined by generalized eigenvalues of the matrix pencil. Unstable regions indicated with dashed lined.

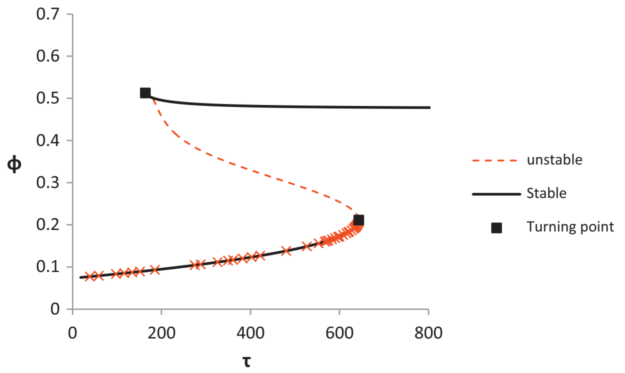

Fig. 2. Stability profile as determined using the underlying ODE. Jacobian determined using central difference formula with $\varepsilon = 10^{-6}$. Points where steady state incorrectly determined to be unstable marked with an '×' symbol.

3. Index reductions and stabilization

3.1. Loss of stability information after index-reduction

In the same manner that Eq. (3) was generated, an explicit expression for the vapor fraction, ϕ, can be written by differentiating Eq. (8) of the reactive flash example with respect to time and combining with Eqs. (6) and (7).

$$\phi = \frac{-\sum_{n-1}^{i=1} f_i(\boldsymbol{x})(K_i - K_n) - f_n(\boldsymbol{x})\left((dK_n/dT)(1 - \sum_{n-1}^{i=1} x_i) + \sum_{n-1}^{i=1} x_i (dK_i/dT)\right)}{\sum_{n-1}^{i=1}((x_i - K_i x_i)/\tau)(K_i - K_n) + ((h_{liq} - h_{vap})/\tau C_p)\left((dK_n/dT)(1 - \sum_{n-1}^{i=1} x_i) + \sum_{n-1}^{i=1} x_i (dK_i/dT)\right)} \qquad (19)$$

where f_i is the vapor-fraction free parts of the differential equations.

$$f_i = \frac{1}{\tau}\left(z_i - x_i - \tau\left(x_i \sum_{j=1}^{r} \nu_{T,j} r_j - \sum_{j=1}^{r} \nu_{i,j} r_j\right)\right), \quad i = 1, \ldots, 3 \qquad (20)$$

$$f_4 = \frac{1}{\tau C_p}\left(h_{feed} + q - h_{liq} - h_{liq}\tau \sum_{j=1}^{r} \nu_{T,j} r_j\right) \qquad (21)$$

Substituting this expression for ϕ into Eqs. (6) and (7) converts the system to an underlying ODE. The same bifurcation path as before was traced as accurately as possible by setting the PITCON absolute and relative error tolerances as well as the minimum step size to the default value of the square root of the machine precision (calculated internally by PITCON to be 2.2×10^{-16}) and setting the maximum step size to be 0.1. The eigenvalues of the reduced system were evaluated at each point, with the jacobian of this reduced system determined using both a central difference formula and an exact analytical expression. (Developing an analytic expression for the jacobian becomes considerably more difficult after the substitution above.) The central-difference step size used for evaluating the jth column of the jacobian was $h = 2\varepsilon(1 + |x_j|)$.

Figs. 2 and 3 show stability curves generated with ε set to 10^{-6} and an exact expression for the jacobian matrix respectively. In both cases, the lower stable portion of the curve was calculated to have a scattered stability pattern with the maximum real part of an eigenvalue being positive along portions of this part of the curve.

If the index-reduced system is written as an index-1 DAE instead of an ODE, the calculated stability profile is still not accurate. The resulting index-1 system is the combination of Eqs. (6) and (7) along with Eq. (19) written in form $\boldsymbol{g}(\boldsymbol{x}) = 0$. In this case, the stability profile is calculated by evaluating the generalized eigenvalues of the index-1 matrix pencil. As can be seen in Fig. 4, the lower stable portion of the curve still incorrectly shows numerous points with unstable steady states.

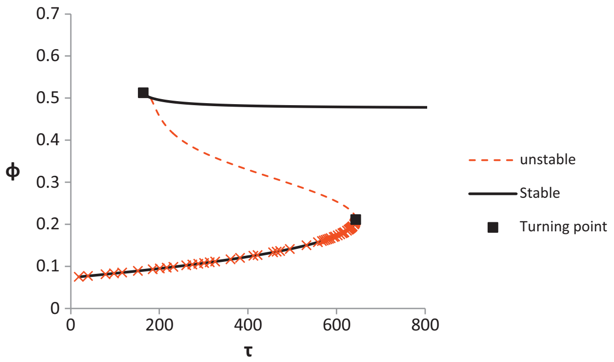

Fig. 3. Stability profile as determined using the underlying ODE. Jacobian determined analytically. Points where steady state incorrectly determined to be unstable marked with an '×' symbol.

The incorrect stability curves shown in Figs. 2–4 are a result of the fact that when the underlying ODE is written in the form of Eq. (3), the jacobian of the linearization is singular at a steady state. More particularly, two propositions are made, which follow simply and directly from those of Riaza (2002, 2004).

Proposition 1. *Given the DAE defined by Eqs. (2a) and (2b) with*

(a) $\boldsymbol{x} \in \mathbb{R}^r, \boldsymbol{y} \in \mathbb{R}^p$

(b) $\boldsymbol{f} : \mathbb{R}^r \to \mathbb{R}^r$, $\boldsymbol{b} : \mathbb{R}^r \to \mathbb{R}^r \times \mathbb{R}^p$, *and* $\boldsymbol{g} : \mathbb{R}^r \to \mathbb{R}^p$, *are at least* C^2 *continous.*

(c) $\left(\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}\right) b(\boldsymbol{x})$ *is of full rank (Eqs. (2a) and (2b) represent DAE in Hessenberg form of size 2)*

If λ *is a generalized eigenvalue of the matrix pencil of the linearization of Eqs. (2a) and (2b) at a steady state* $(\boldsymbol{x}^*, \boldsymbol{y}^*)^{\mathrm{T}}$, *then* λ *is an eigenvalue of the jacobian of the right hand side of Eq. (3) at* $\boldsymbol{x}^*$.

Proof. Write the matrix pencil defined by the linearization of Eqs. (2a) and (2b) as

$$\lambda A_2 - J_2^* = \lambda \begin{pmatrix} I_r & 0 \\ 0 & 0 \end{pmatrix} - \begin{pmatrix} (f + by)_x & b \\ g_x & 0 \end{pmatrix}_{(x^*, y^*)^T} \qquad (22)$$

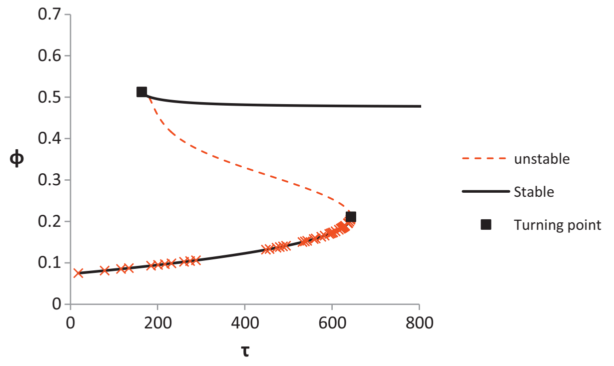

Fig. 4. Stability profile as determined using the underlying index-1 DAE. Jacobian determined analytically. Points where steady state incorrectly determined to be unstable marked with an '×' symbol.

Similarly, the matrix pencil of the linearization of the system defined by (2a) and (2c) can be written as

$$\lambda A_1 - J_1^* = \lambda \begin{pmatrix} I_r & 0 \\ 0 & 0 \end{pmatrix} - \begin{pmatrix} (f+by)_x & b \\ g_x(f+by)_x & g_x b \end{pmatrix}_{(x^*,y^*)^T} \tag{23}$$

noting that this matrix pencil is being evaluated at a steady state and that both $(\boldsymbol{f}(\mathbf{x}^*)+\boldsymbol{b}(\mathbf{x}^*)\boldsymbol{y}^*)$ and $\boldsymbol{g}(\mathbf{x}^*)$ are zero. Finally, the jacobian of the ODE defined by Eq. (3) at steady state can be written as

$$J_0^* = \left(f_x - (b(g_x b)^{-1} g_x f)_x\right)_{(x^*,y^*)^T} \tag{24}$$

The condition that $(\partial \boldsymbol{g}/\partial \boldsymbol{x})\boldsymbol{b}$ be non-singular implies that the DAE defined by Eqs. (2a) and (2c) is of index-1. Riaza (2002) has shown that the spectrum of eigenvalues of the matrix pencil of this index-1 DAE, $\sigma(A_1, J_1^*)$ is identical to the spectrum of eigenvalues of the jacobian of Eq. (3), $\sigma(J_0^*)$. Therefore, it is sufficient to show that $\sigma(A_2, J_2^*) \subset \sigma(A_1, J_1^*)$

If λ is an eigenvalue of the linearization of Eqs. (2a) and (2b), then

$$\left(\lambda \begin{pmatrix} I_r & 0 \\ 0 & 0 \end{pmatrix} - \begin{pmatrix} (f+by)_x & b \\ g_x & 0 \end{pmatrix}_{(x^*,y^*)^T}\right) \begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = 0 \tag{25}$$

for some eigenvector $(w_1, w_2)^{\mathrm{T}}$. Therefore

$$\lambda w_1 = (f+by)_x^* w_1 + b w_2 \tag{26a}$$

$$0 = g_x^* w_1 \tag{26b}$$

Multiplying Eq. (26b) by λ and substituting in Eq. (26a) results in

$$0 = g_x^*(f+by)_x^* w_1 + g_x^* b^* w_2 \tag{26c}$$

Re-arranging (26a) and (26c) implies that

$$\left(\lambda \begin{pmatrix} I_r & 0 \\ 0 & 0 \end{pmatrix} - \begin{pmatrix} (f+by)_x & b \\ g_x(f+by)_x & g_x b \end{pmatrix}_{(x^*,y^*)^T}\right) \begin{pmatrix} w_1 \\ w_2 \end{pmatrix}$$

$$= (\lambda A_1 - J_1^*) \begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = 0 \tag{27}$$

and hence that $\sigma(A_2, J_2^*) \subset \sigma(A_1, J_1^*) = \sigma(J_0^*)$. □

Proposition 2. *The spectrum of eigenvalues of the jacobian of Eq. (3), $\sigma(J_0^*)$, contains at least p null eigenvalues at a steady state, where p is the dimension of **y**.*

Proof. Eqs. (2a) and (2d) represent the underlying ODE generated by two successive differentiations of the algebraic constraint. Moving the term for $d\boldsymbol{y}/dt$ to the left hand side, the matrix pencil of the system linearization at a steady state $(\boldsymbol{x}^*, \boldsymbol{y}^*)^{\mathrm{T}}$ can be written as

$$\lambda A_U - J_U^* = \lambda \begin{pmatrix} I_r & 0 \\ 0 & g_x b \end{pmatrix}_{(x^*,y^*)^T} - \begin{pmatrix} (f+by)_x & b \\ -g_x(f+by)_x^2 & -g_x(f+by)_x b \end{pmatrix}_{(x^*,y^*)^T} \tag{28}$$

Proposition 5 of Riaza (2002) states that the spectrum of this matrix pencil contains at least $2p$ null eigenvalues. It is straightforward to show that $\sigma(J_0^*) = \sigma(A_1, J_1^*) \subset \sigma(A_U, J_U^*)$ using the same method as Proposition 1. As the rank of J_0^* is $\leqq r$ (the dimension of $\boldsymbol{x}$), $\sigma(J_0^*)$ contains at least p null eigenvalues. □

Therefore, when analyzing the eigenvalues of the reactive flash defined by Eqs. (6), (7), and (19)–(21), the dimension of $\boldsymbol{y}$ is 1, and a single eigenvalue with the lowest absolute value should be discarded. When this is carried out, the correct stability profile shown in Fig. 1 is obtained in all the cases described previously.

It is important to note that tracking the orbit of these equations with a standard initial-value problem solver such as MATLAB's ode15s will result in serious numerical difficulties at a steady state due the presence of a singular jacobian matrix there.

3.2. Stabilization of the index-reduced system

Tracing the solution path of an Initial Value Problem that has been index-reduced is subject to the so-called 'drift' phenomena. The drift in question arises due to the fact that the original algebraic constraints are lost, and any local errors can be compounded by integration. One method to address this problem is to project back onto the original algebraic constraint at each time step (Ascher & Petzold, 1991). The other widely used method is to stabilize the invariant manifold defined by the algebraic equations using the technique of Baumgarte (1972). This technique has been adapted further by Ascher, Chin, and Reich (1994) and Chin (1995). Here, these techniques are used primarily to stabilize the index reduced system at the steady states.

As discussed previously, a DAE in the form of Eqs. (2a) and (2b) can be written as an ODE after one differentiation.

$$\boldsymbol{x}' = \boldsymbol{f}(\boldsymbol{x}) - \boldsymbol{b}(\boldsymbol{x})\left(\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}\boldsymbol{b}(\boldsymbol{x})\right)^{-1}\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}\boldsymbol{f}(\boldsymbol{x}) \equiv \boldsymbol{F}_0(\boldsymbol{x}) \tag{29}$$

The stabilized form of this equation is written as

$$x' = \boldsymbol{F}_0(\boldsymbol{x}) - \gamma \boldsymbol{S}(\boldsymbol{x})\boldsymbol{g}(\boldsymbol{x}) \tag{30}$$

where the real valued stabilization factor γ is greater than zero and the function $\boldsymbol{S}(\boldsymbol{x})$ meets the requirement that $(\partial \boldsymbol{g}/\partial \boldsymbol{x})\boldsymbol{S}(\boldsymbol{x})$ be symmetric positive definite and also that it have *positive* (non-zero) eigenvalues. Some choices for $\boldsymbol{S}(\boldsymbol{x})$ are

$$\boldsymbol{S}(\boldsymbol{x}) = \boldsymbol{b}(\boldsymbol{x})\left(\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}\boldsymbol{b}(\boldsymbol{x})\right)^{-1} \tag{31}$$

$$\boldsymbol{S}(\boldsymbol{x}) = \frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}^{\boldsymbol{T}}\left(\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}^{\boldsymbol{T}}\right)^{\boldsymbol{-1}} \tag{32}$$

$$\boldsymbol{S}(\boldsymbol{x}) = \frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}^{\boldsymbol{T}} \tag{33}$$

Eq. (31) is the classic Baumgarte stabilization, whereas Eqs. (32) and (33) were proposed by Chin (1995). In the case of the first two, $(\partial \boldsymbol{g}/\partial \boldsymbol{x})\boldsymbol{S}(\boldsymbol{x})$ is simply the identity matrix, and trivially meets requirements of symmetric positive definiteness and positive eigenvalues. However, using Eq. (33) requires that $(\partial \boldsymbol{g}/\partial \boldsymbol{x})$ have full rank.

To numerically implement the stabilization techniques, the ODE in Eq. (30) can be considered, or alternatively, an index-1 system defined by

$$x' = \boldsymbol{F}_0(\boldsymbol{x}) \tag{34a}$$

$$0 = \frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}(\boldsymbol{f}(\boldsymbol{x}) + \boldsymbol{b}(\boldsymbol{x})\boldsymbol{y}) + \gamma \boldsymbol{S}(\boldsymbol{x})\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}\boldsymbol{g}(\boldsymbol{x}) \tag{34b}$$

Eq. (34b) is obtained by differentiating the algebraic constraint $0 = \boldsymbol{g}(\boldsymbol{x})$, substituting in Eq. (30), and noting that $(\partial \boldsymbol{g}/\partial \boldsymbol{x})\boldsymbol{F}_0(\boldsymbol{x}) = 0$. The need for requiring that $(\partial \boldsymbol{g}/\partial \boldsymbol{x})\boldsymbol{S}(\boldsymbol{x})$ be symmetric positive definite and have positive eigenvalues becomes clear when (34b) is rewritten as

$$\frac{d\boldsymbol{g}}{dt} = -\gamma \boldsymbol{S}(\boldsymbol{x})\frac{\partial \boldsymbol{g}}{\partial \boldsymbol{x}}\boldsymbol{g}(\boldsymbol{x}) \tag{35}$$

and the derivative of the Lyapunov function $\boldsymbol{L}(\boldsymbol{x}) = (1/2)\boldsymbol{g}^T(\boldsymbol{x})\boldsymbol{g}(\boldsymbol{x})$ over Eq. (29) is evaluated. It can then be shown that this derivative is negative in a region around $\boldsymbol{x}$, and consequently that the invariant manifold defined by $\boldsymbol{g}(\boldsymbol{x}) = 0$ is asymptotically stable. (See Chin (1995) for further details.)

For the reactive flash being considered here, stabilization of Eqs. (31) and (33) were tested at the steady state solutions. With $\gamma = 1$ in all cases, both the index-1 and ODE formulation predicted the identical stability profile shown in Fig. 1, eliminating all previous errors caused by the zero-valued eigenvalue. Both stabilizations were seen to greatly improve the condition number of the jacobian matrix. At a stable point close to the lower turning point, the unstabilized jacobian had a condition number of 1.38×10^{11} and a determinant of 2.90×10^{-21}. With $\gamma = 1$, Eq. (31) reduced the condition number to 9.29×10^6 and Eq. (33) reduced it to 7.31×10^7. The same stabilizations increased the determinant to 2.55×10^{-11} and 2.00×10^{-10}, respectively, effectively increasing the rank of the jacobian matrix from 3 to 4.

Values of γ from 0.1 to 1×10^5 were tested. In the case of stabilization Eq. (31), all values of γ in this range were successful for both the index-1 and ODE representations and for the numerical and analytical jacobians. For stabilization Eq. (33) used with the index-1 formulation, values of γ in the range [0.1, 1×10^5] were also successful. However, for the ODE formulation, the predicted stability was calculated to extend very slightly beyond the upper turning point when γ was greater than 1000. Fig. 5 shows the calculated stability profile using $\gamma = 5000$ and with the jacobian evaluated using central differences with $\varepsilon = 10^{-10}$. It can be seen by comparing Figs. 5 and 4 that while the results are considerably more accurate, the choice of γ cannot be entirely arbitrary. A simple algorithm to determine a suitable value for γ is as follows:

(a) Generate stabilized path with initial value of $\gamma^0 = 1.0$
(b) Re-generate the same path with $\gamma^0/4$ and $4\gamma^0$.
(c) If the predicted stability profiles are not identical, set $\gamma^0 = 2\gamma^0$ and return to step (a). Otherwise, accept γ^0 as an appropriate choice.

4. An alternative generalized index reduction

When considering an adiabatic, constant pressure flash with an isomerization reaction A → B, Rodriguez et al. (2001) obtained an expression for the dynamic evolution of the vapor fraction ϕ by exploiting the fact that the liquid (and vapor) mole fractions could be written as a function of temperature alone. This technique can be generalized to the n component, r reaction system defined by Eqs. (6)–(8) by first noting that x_{n-1} can be written as a function of $T, P, x_{1.}x_{n-2}$. Therefore, at constant pressure, the time derivative of x_{n-1} can be written as

$$\frac{dx_{n-1}}{dt} = \frac{\partial x_{n-1}}{\partial x_1}\frac{dx_1}{dt} + \frac{\partial x_{n-1}}{\partial x_2}\frac{dx_2}{dt} + \cdots + \frac{\partial x_{n-1}}{\partial x_{n-2}}\frac{dx_{n-2}}{dt} + \frac{\partial x_{n-1}}{\partial T}\frac{dT}{dt} \tag{36}$$

Substituting Eqs. (6) and (7) into (36), first noting that Raoult's law dictates that

$$\frac{\partial x_{n-1}}{\partial x_j} = \frac{K_n - K_j}{K_{n-1} - K_n} \tag{37}$$

$$\frac{\partial x_{n-1}}{\partial T} = \frac{(K_{n-1} - K_n)(-(dK_n/dT) + \sum_{n-2}^{i=1}((dK_n/dT) - (dK_i/dT)))}{(K_{n-1} - K_n)^2} - \frac{(1 - K_n + \sum_{n-2}^{i=1} x_i(K_n - K_i))((dK_{n-1}/dT) - (dK_n/dT))}{(K_{n-1} - K_n)^2} \tag{38}$$

allows the following equation to be generated, which is solved to obtain an expression for ϕ

$$\begin{aligned}
&\frac{1}{\tau}\left(z_{n-1} - x_{n-1} - \phi(K_{n-1}x_{n-1} - x_{n-1}) - \tau\left(x_{n-1}\sum_{j=1}^{r} \upsilon_{T,j}r_j - \sum_{j=1}^{r} \upsilon_{i,j}r_j\right)\right) \\
&= \frac{\partial x_{n-1}}{\partial x_1}\frac{1}{\tau}\left(z_1 - x_1 - \phi(K_1x_1 - x_1) - \tau\left(x_1\sum_{j=1}^{r} \upsilon_{T,j}r_j - \sum_{j=1}^{r} \upsilon_{1,j}r_j\right)\right) + \cdots \\
&+ \frac{\partial x_{n-1}}{\partial x_{n-2}}\frac{1}{\tau}\left(z_{n-2} - x_{n-2} - \phi(K_{n-2}x_{n-1} - x_{n-2}) - \tau\left(x_{n-2}\sum_{j=1}^{r} \upsilon_{T,j}r_j - \sum_{j=1}^{r} \upsilon_{n-2,j}r_j\right)\right) \\
&+ \frac{\partial x_{n-1}}{\partial T}\frac{1}{\tau C_p}\left(\left(h_{feed} + q - h_{liq} - h_{liq}\tau\sum_{j=1}^{r} \upsilon_{T,j}r_j\right) + \frac{\phi}{\tau C_p}(h_{liq} - h_{vap})\right)
\end{aligned} \tag{39}$$

When applied to the ethylene glycol reactive flash example, the resulting system is an ODE in three variables, x_A, x_B and T. (For all index-reductions carried out here, a valuable error check is available by comparing the vapor fraction of the original system and the one solved for during the system reduction. In all cases tested here, they were found to be identical to at least 10 digits of accuracy.) The dimension of this ODE is appropriate for the original index-2 system and it is unnecessary to discard any eigenvalues when using it to check stability.

Figs. 6 and 7 show the predicted stability profile generated when the path is tracked with the same variables as in the previous section and with the jacobian evaluated with the central difference formula using ε values of 10^{-6} and 10^{-8}. As can be seen in these graphs, the resulting stability profile inaccurately extends the region of stability beyond the lower turning point. When the jacobian is determined analytically (again requiring considerable effort), the correct stability profile is generated. It is interesting to note that in regions where the numerically generated jacobian with $\varepsilon = 10^{-8}$ incorrectly predicted stability, the maximum relative error in the jacobian was less than 2×10^{-8}. As with the index reduction in the previous section, the resulting jacobian was very badly conditioned. Unfortunately, the stabilizations used previously do not apply to this index reduction.

Numerical evidence of the instability of steady states with a positive real eigenvalue is provided when the orbit of the index-2 system is tracked using APMonitor (Hedengren, 2012). Fig. 8 contains the dynamic profile generated from the three steady states at $\tau = 500$ when feed rate is suddenly increased so that the time constant is reduced to 480. As expected, the upper and lower steady states move to the corresponding steady states nearby, whereas

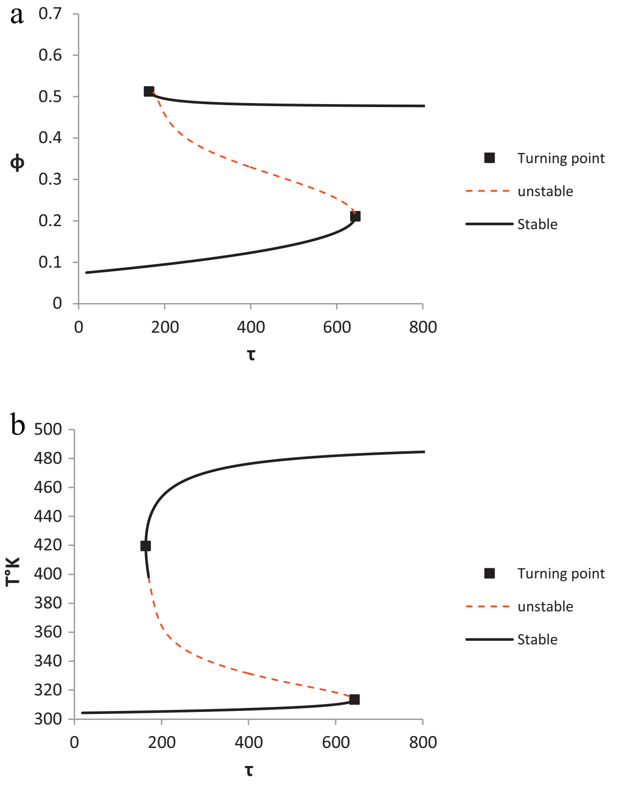

Fig. 5. (a and b) ODE formulation. Jacobian via central difference with $\varepsilon = 10^{-10}$. Stabilization using Eq. (33) with $\gamma = 5000$. Temperature curve shows that the predicted set of stable solutions incorrectly moves beyond turning point at this large value of γ.

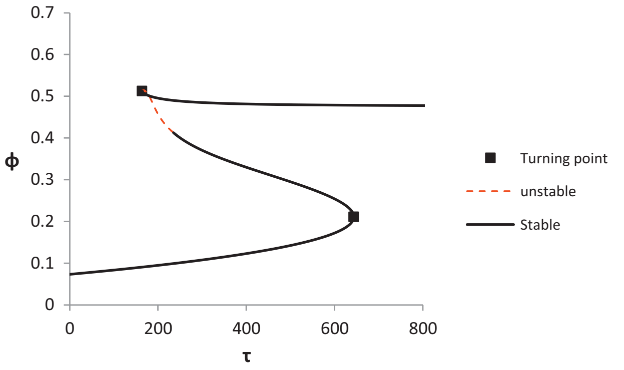

Fig. 6. ODE generated by 'Rodriguez' index reduction. Jacobian via central difference formula with $\varepsilon = 10^{-6}$.

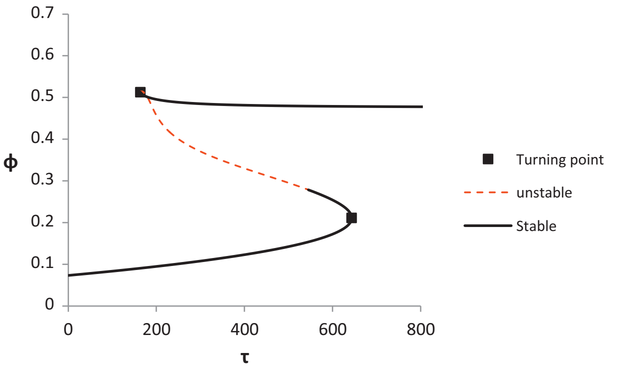

Fig. 7. ODE generated by 'Rodriguez' index reduction. Jacobian via central difference formula with $\varepsilon = 10^{-8}$.

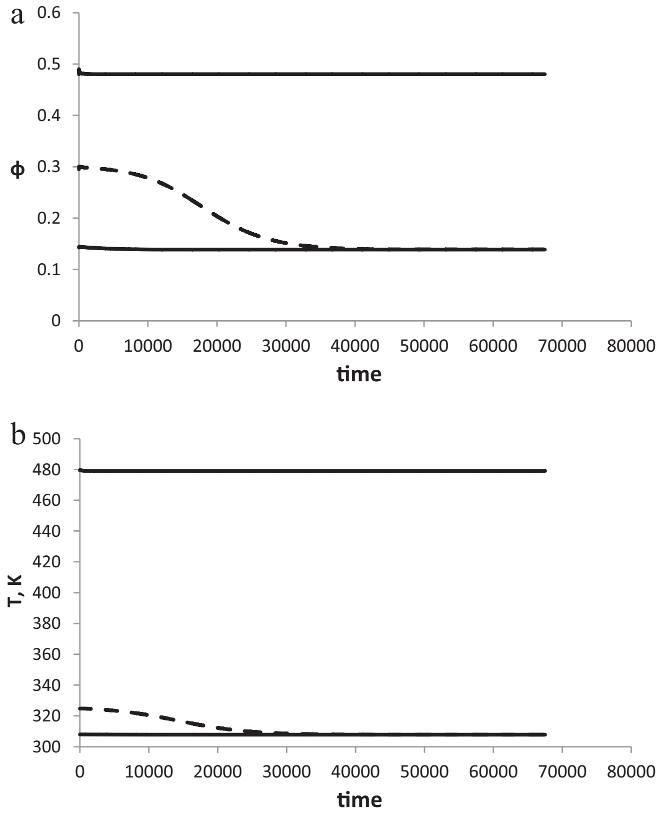

Fig. 8. (a and b) Dynamic evolution of reactive flash from steady states at $\tau = 500$ to new steady state at $\tau = 480$.

the middle steady state falls to the lower steady state on a different segment of the bifurcation path. This middle solution was incorrectly predicted by index reduction methods to be stable in Figs. 6 and 7.

5. Reactive distillation example

Direct evaluation of system stability for a larger reactive distillation model can be demonstrated with an idealized three-component reactive distillation model presented by Luyben and Yu (2008). The reversible reaction under consideration was $A + B \rightleftharpoons C$.

The base case column consisted of 16 total stages, including the reboiler and condenser. As the desired product C was the heaviest of the three, the column was operated at infinite reflux, essentially reducing the degrees of freedom for column operation to 1. The reaction was confined to occur in stages 2–10 only (with condenser labeled as stage 1) by specifying the molar holdup as 1000 mol on these stages and zero elsewhere. Reaction rate on each stage is given by

$$\begin{aligned} r_j &= k_{fwd} x_A x_B - k_{rev} x_C \\ k_{fwd} &= 6.73624 \times 10^{15} \exp\left(-\frac{30}{R_g T_j}\right) \\ k_{rev} &= 3.18051 \times 10^{20} \exp\left(-\frac{40}{R_g T_j}\right) \end{aligned} \tag{40}$$

The reaction rate equation above requires that the equilibrium constant K_{eq}, has a value of 20.0 at $T = 366$ K. The activation energies of the forward and reverse reactions are 30 and 40 kcal/mol, respectively and the heat of reaction is -10 kcal/mol.

Table 2
Data used for reactive distillation model.

	A	*B*	*C*
Antoine coeff. $A_j(p^{SAT}\text{ bar}) = A - B/(T^\circ K)$	12.34	11.65	10.96
Antoine coeff. B_j	3862	3862	3862
Heat of formation (kcal/mol)	0	0	−10
Heat of vaporization (kcal/mol)	6.944	6.944	6.944
Feed rate to column (mol/s)	12.63	12.82	0
Feed stage location	10	2	–

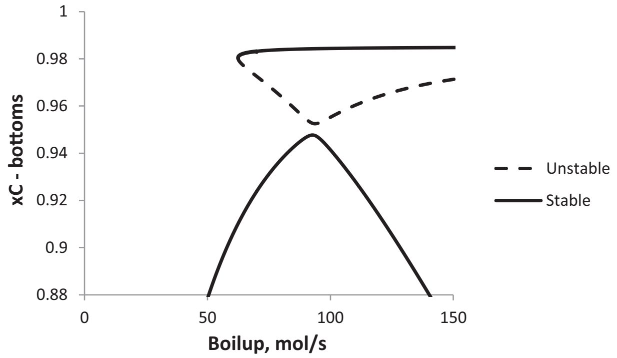

Fig. 9. Steady state stability profile of reactive distillation model.

Feeds of component *A* and *B* are not quite equimolar, but set at 12.63 mol/s and 12.82 mol/s, respectively. Vapor–liquid equilibrium is evaluated using Raoult's law and the specific enthalpy is calculated using Eqs. (17) and (18) with sensible heat neglected in both the vapor and liquid phases. Table 2 contains the remaining data used to determine a steady state for their base case.

The molar boilup required to obtain the stated target component mole fraction of *C* of 0.98 was calculated to be 62.476 mol/s (compared to a value of 62.03 given by Luyben & Yu (2008)). Fixing the boilup at this rate, and solving the set of nonlinear equations using a global Newton homotopy method resulted in two additional steady states being identified with mole fraction of component *C* in the bottoms exit stream of 0.9806 and 0.9102.

To identify the stability of these steady states, the generalized eigenvalues of the matrix pencil were evaluated at these steady states. As the liquid heat capacity and the liquid holdup of the nonreactive stages were both set to zero and the liquid holdup on the reactive stages is constant, the only dynamic equations for this system are the mass balances for components A and B on the reactive stages. Using the standard MESH equations the dynamic representation of this column is an index-2 DAE containing 18 differential equations and 126 algebraic constraints.

Fig. 9 shows the stability profile across a range of reboiler boilup rates. The maximum real value of the generalized eigenvalues at each steady state was seen to change sign at the turning point on the upper segment of the graph, and remained negative on the entire lower unconnected segment. This would suggest that this theoretical column could fall from the desired high conversion steady state to a stable lower conversion segment of the path if the boilup rate was reduced below 62.44 mol/s. The stability of this lower segment would eliminate the possibility of returning to the high conversion steady state by simply increasing the boilup rate again, but would instead require a reduction of the feed rate of both A and B.

6. Conclusions

The most robust and accurate method to determine the stability of a steady state of an index-2 DAE in Hessenberg form is to directly evaluate the generalized eigenvalues of the linearized system. This can be carried out by steady state simulators without the need for any dynamic modeling. This method was applied to specific reactive flash and reactive distillation problems to accurately identify stable and unstable steady states. The equations presented to model reactive flash and reactive distillation problems are in Hessenberg form regardless of the number of chemical species or the number of chemical reactions or their stoichiometry. When an index-2 DAE is reduced to an ODE by a single differentiation as in Section 3, the resulting jacobian matrix will have a null eigenvalue at every steady state with multiplicity of at least the dimension of $\boldsymbol{y}$ (the implicit time varying variable). These null eigenvalues must be accounted for when determining the stability of a steady state. The ill-conditioning caused by the null eigenvalues can be substantially improved by applying one of the stabilization methods described in Section 3.1. These stabilizations are not applicable when the index reduction is obtained by alternative differentiations such as that described in Section 4. While this index-reduction does not necessarily have a null eigenvalue at a steady state, the problems generated by badly conditioned jacobians still exist, with even minor errors in this matrix resulting in incorrect stability predictions.

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