

# Steady State Multiplicity and Stability in a Reactive Flash

Iván E. Rodríguez, Alex Zheng and Michael F. Malone\*  
Department of Chemical Engineering  
University of Massachusetts  
Amherst, MA 01003

## Abstract

In this paper, we study the steady state solutions and their stability for an isobaric, adiabatic reactive flash. We show that the presence of vapor-liquid equilibrium can remove or create steady state multiplicity. For example, a system that does not have multiple steady states in a one phase CSTR can display multiple steady states as a two phase reactive flash unit. Both input multiplicity and output multiplicity are possible. Some of the multiplicities can be observed within the reactive flash operation. Others are observed when combining the operation of the reactive flash with the one phase CSTR. The existence of multiple steady states and their stability properties are related to a dimensionless quantity that depends on the heats of reaction and vaporization as well as the vapor-liquid equilibrium behavior. Three typical examples are shown.

The effect of reflux is also studied by adding a condenser for an exothermic reaction. This system can display multiple steady states with respect to the reflux ratio. At a sufficiently large reflux ratio, the system eventually ceases to display steady state multiplicity.

## Keywords

Reactive distillation, Stability, Multiple steady states

## Introduction

Reactive distillation (RD) systems combine chemical reaction and distillation, which are traditionally done separately. Hybrid combinations also include catalytic distillation, reactive extraction, phase-transfer catalysis, etc. By combining different unit operations into one consolidating system (whenever feasible), one could take advantage of the properties of one operation to enhance the others and sometimes improve the profitability of the overall process. As stated by Doherty and Malone (2001, page 427): "Reactive or catalytic distillation has captured the imagination of many recently because of the demonstrated potential for capital productivity improvements (from enhanced overall rates, by overcoming very low reaction equilibrium constants, and by avoiding or eliminating difficult separations), selectivity improvements (which reduce excess raw materials use and byproduct formation), reduced energy use, and the reduction or elimination of solvents."

Dynamic modeling of RD columns has received attention recently. Early studies were based on models that included the material balances and simultaneous phase and reaction equilibrium (e.g., Grosser et al. (1987)). More recent work has involved more complex models involving material and energy balances and kinetically controlled reactions (e.g., Alejski and Duprat (1996); Kumar and Daoutidis (1999)). Despite significant progress on design and dynamic modeling of reactive distillation systems, more general results are needed concerning the steady state and dynamic behavior of RD systems. Steady state multiplicity has been demonstrated for spe-

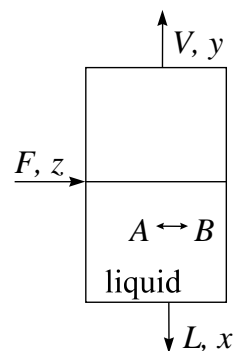


Figure 1: Diagram of a reactive flash.

cific RD systems (e.g., Ciric and Miao (1994); Kumar and Daoutidis (1999); Hauan et al. (1997)). Some of the causes of steady state multiplicity have been established for the case of simultaneous reaction and phase equilibrium (Güttinger and Morari (1999)), but this is not the case for kinetically controlled RD systems. This paper establishes some of the conditions under which the steady state multiplicity is possible in a simple model system. The current work focuses on a simple RD system, the isobaric, adiabatic flash with chemical reaction for a binary mixture. We assume mass-transfer rates between the liquid and the vapor to be fast when compared to other characteristic times in the system; therefore the vapor composition is in equilibrium with the liquid composition at all times.

## The Reactive Flash

Figure 1 shows a graphical representation of the reactive flash system. An exothermic isomerization reaction

\*To whom correspondence should be addressed. Address: 154A Goessmann Laboratory, 686 North Pleasant Street, Amherst, MA 01003-9303. Telephone: (413) 545-0838. Fax: (413) 545-1133. E-mail: mmalone@ecs.umass.edu

occurs in the liquid phase ( $A \rightleftharpoons B$ ) only. The reactant is the heavier component. Both phases are assumed to be well mixed. Including the energy balance along with the overall mass balance and the species balance (for the reactant) yields:

$$\frac{dH}{dt} = F - V - L \quad (1)$$

$$\tau \frac{dx}{dt} = z - x - \phi(y - x) - \tau r \quad (2)$$

$$\tau C_p \frac{dT}{dt} = \tau r (-\Delta H_{rxn}) - C_p(T - T_i) - \phi(\Delta H_{vap}) \quad (3)$$

In these equations,  $H$  is the molar liquid holdup,  $F$  is the molar feed flowrate,  $L$  is the liquid molar flowrate out of the reactor,  $V$  is the vapor molar flowrate out of the reactor,  $t$  is the time, and  $x$  and  $y$  are the mole fractions of reactant  $A$  in the liquid and the vapor, respectively.  $T_i$  and  $z$  are the feed's temperature and mole fraction of  $A$ , respectively. Meanwhile,  $T$  is the temperature of the reactive flash and  $C_p$  is the liquid heat capacity (which has been assumed to be constant). The reaction rate is given by  $r$  which has units of  $(time)^{-1}$ . The fraction of the feed that leaves as vapor is defined as  $\phi$  ( $= V/F$ ). The residence time is given by  $\tau$  ( $= H/F$ ).

## Steady State Behavior

If one considers the mass-transfer within the phases to be relatively fast, then one can relate the compositions of the phases by a vapor-liquid equilibrium relationship. Since the system is isobaric, knowing either  $T$ ,  $x$  or  $y$  allows one to determine the other two quantities. One could use one of the balances, Equation 2 or Equation 3, to calculate  $T$  and the other one to determine the value of  $\phi$ . For example,

$$0 = \frac{Da \cdot r}{k_{ref}} (-\Delta H_{rxn}) - C_p(T - T_i) - \phi(\Delta H_{vap}) \quad (4)$$

$$\phi = \frac{z - x + \frac{C_p(T_i - T)}{-\Delta H_{rxn}}}{\frac{\Delta H_{vap}}{-\Delta H_{rxn}} + y - x} \quad (5)$$

$$\Lambda \equiv \frac{\Delta H_{vap}}{-\Delta H_{rxn}} + y - x \quad (6)$$

In Equation 4, the Damköhler number,  $Da$  (Damköhler, 1939) is defined as the ratio of the residence time to a characteristic reaction time,  $Da = \frac{\tau}{1/k_{ref}}$ . The characteristic reaction time is given by the reciprocal of the forward reaction rate constant evaluated at a reference temperature,  $k_{ref}$ . From Equation 4, we have

$$\frac{dT}{dDa} = \frac{-\Delta H_{rxn} \cdot r / k_{ref}}{C_p + \frac{d(\phi \Delta H_{vap})}{dT} - Da(-\Delta H_{rxn} / k_{ref}) \frac{dr}{dT}} \quad (7)$$

The steady state characteristics of this equation can be obtained by studying its denominator (since its numerator is always positive). After some manipulations,

the denominator of this equation becomes

$$\left[ (y - x)C_p - \frac{dr}{dT} Da(-\Delta H_{rxn}\Lambda) / k_{ref} + \frac{d\Delta H_{vap}}{dT} (y - x)\phi - \left( \phi \frac{dy}{dT} + (1 - \phi) \frac{dx}{dT} \right) \Delta H_{vap} \right] 1/\Lambda \quad (8)$$

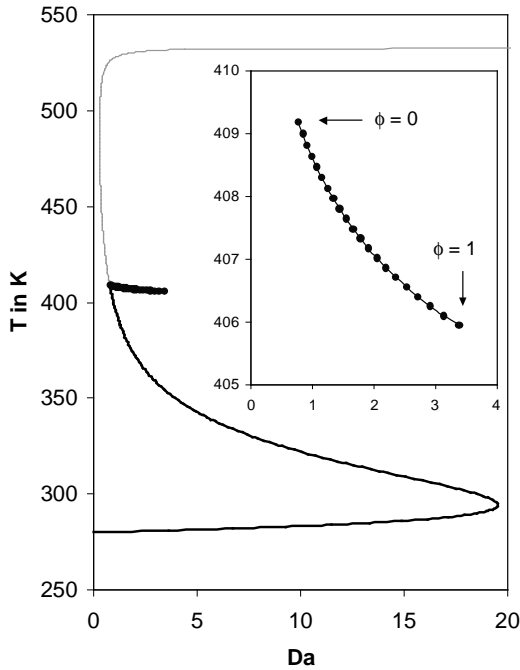
Some isomerizations are exothermic with large heats of reaction (see Frenkel et al. (1993) for examples). One example of such a reaction is the isomerization of quadricyclane to norbornadiene. Its heat of reaction has been measured to be around  $-\Delta H_{rxn} = 89,000$  J/mol while the heat of vaporization of the two compounds lie in the range of 34,830 to 37,850 J/mol (An and Xie (1993)). In the examples that follow, the heat released by the reaction is used to heat the system and vaporize part of the reacting mixture. The heat of reaction ( $-\Delta H_{rxn}$ ) is assumed to be greater than the heat of vaporization of the mixture ( $\Delta H_{vap}$ ). Also, since the mole fractions correspond to those of the heavier component the value of  $\Lambda$  can be either positive or negative depending on the particular properties of a given system.

### Case 1: $\Lambda > 0$

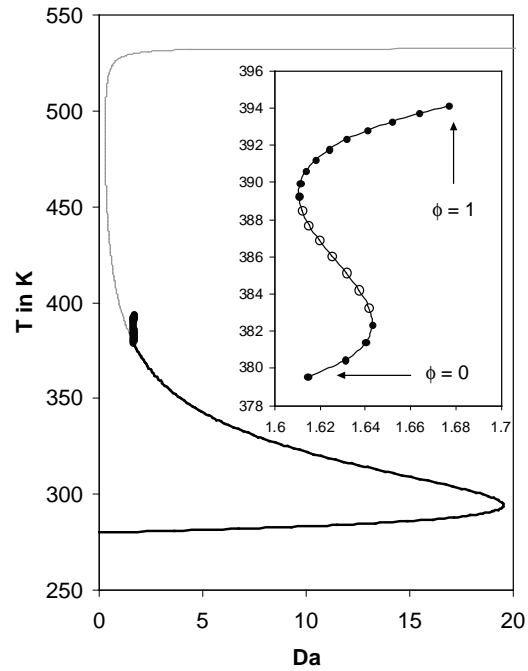
The mole fractions in Expression 8 are those of the heavier component, therefore  $y - x < 0$  (for systems without an azeotrope) and the first term in expression (8) is negative. Since  $\frac{dx}{dT} > 0$ ,  $\frac{dy}{dT} > 0$ , and  $0 \leq \phi \leq 1$ , the last term is negative. Since the reaction rate generally increases with the temperature (i.e.,  $\frac{dr}{dT} > 0$ ) and  $\Lambda > 0$ , the second term is negative. The third term involves  $\frac{d\Delta H_{vap}}{dT}$ . If the value of the heat of vaporization is approximately constant for the temperature range of interest, then  $\frac{d\Delta H_{vap}}{dT} \approx 0$ . Therefore, if  $\Lambda > 0$ , then expression (8) is negative. Since the sign of Equation 7 depends on the sign of its denominator, then  $\frac{dT}{dDa} < 0$  and there is only one steady state for each  $Da$  within the two phase region. It can also be shown that this steady state is stable (Rodríguez et al., 2001).

Figure 2 shows the temperature for a case with  $\Lambda > 0$  (parameters are given in Table 1). Here, a case with a small relative volatility and a small ratio  $\frac{\Delta H_{vap}}{-\Delta H_{rxn}}$  is depicted. The two phase region starts at  $\phi = 0$  and ends at  $\phi = 1$ , after which steady state solutions are infeasible with the current setup. The small relative volatility ensures that  $\Lambda > 0$  and a single steady state exists within the two phase region.

The one phase adiabatic CSTR steady states are also shown for comparison. All of those steady states (CSTR) are attainable at high pressures such that the system does not boil. If one decreases the pressure and allows the system to reach a boiling point, then one starts to move along the two phase region trajectory. Therefore, the CSTR states that lie above the two phase region are



**Figure 2:** Temperature as a function of the Damköhler number for a CSTR and a reactive flash (also as inset). A system that displays multiple steady states as a CSTR only displays a single steady state as a reactive flash.



**Figure 3:** The reactive flash (also as inset) displays output multiplicity within the two phase region as well as with the CSTR operation.

Quantity	Description	Value
$k_0$	Pre-exponential factor	1000 (1/s)
$E_a/R$	Activation energy/ universal gas constant	6362 (K)
$K_{eq}$	Equilibrium constant	$1.4843 \exp[117.7 (1/T - 1/298)]$
$r$	Reaction rate law	$k[x - \frac{1-x}{K_{eq}}]$ (1/s)
$C_p$	Liquid heat capacity	252 (J/mol K)
$T_i$	Feed Temperature	280 (K)
$z$	Mole fraction of A in the feed	1
Figure 2		
$\alpha$	Relative volatility	2
$\Delta H_{vap}$	Heat of vaporization	36,600 (J/mol)
$-\Delta H_{rxn}$	Heat of reaction	115,000 (J/mol)
Figure 3		
$\alpha$	Relative volatility	12
Figure 4		
$\Delta H_{vap}$	Heat of vaporization	9,900 (J/mol)
$-\Delta H_{rxn}$	Heat of reaction	25,000 (J/mol)
Figures 5 and 6		
$\Delta H_{vap}$	Heat of vaporization	36,622 (J/mol)
$-\Delta H_{rxn}$	Heat of reaction	155,000 (J/mol)

**Table 1:** Values used for the examples.

no longer accessible at this lower pressure (light colored line).

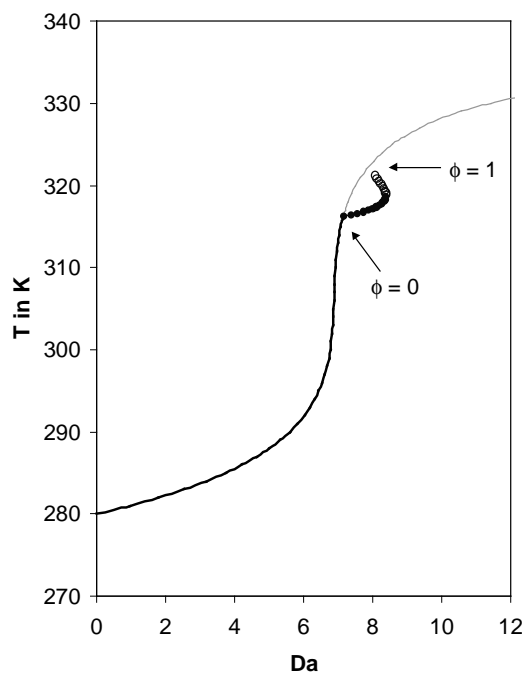
Comparing the one phase and two phase regions simultaneously one can see that there is the possibility of input multiplicity for this system. The behavior of the system in those two regions is significantly different, as is the required control policy for each case. If one is measuring temperature to control the system then it is important to be aware of this characteristic of the system as it affects the required control strategy.

### Case 2: $\Lambda < 0$

If  $\Lambda < 0$ , the second term inside the brackets in expression (8) changes sign and becomes positive. This means that expression (8) and consequently  $\frac{dT}{dDa}$  could change sign and result in multiple steady states. If the slope,  $\frac{dT}{dDa}$ , is positive the system is stable and unstable otherwise (Rodríguez et al., 2001).

Figure 3 shows the results of such a case. In this situation, a system with a higher relative volatility is depicted. The value of  $\Lambda$  is negative and one can observe the appearance of multiple steady states within the two phase region. The lower and upper branches of steady states are stable and the middle one is unstable.

When  $\Lambda < 0$ , the temperature increases as the system goes from  $\phi = 0$  to  $\phi = 1$ . In doing so, there is a multi-directional enhancement in the reaction rate for



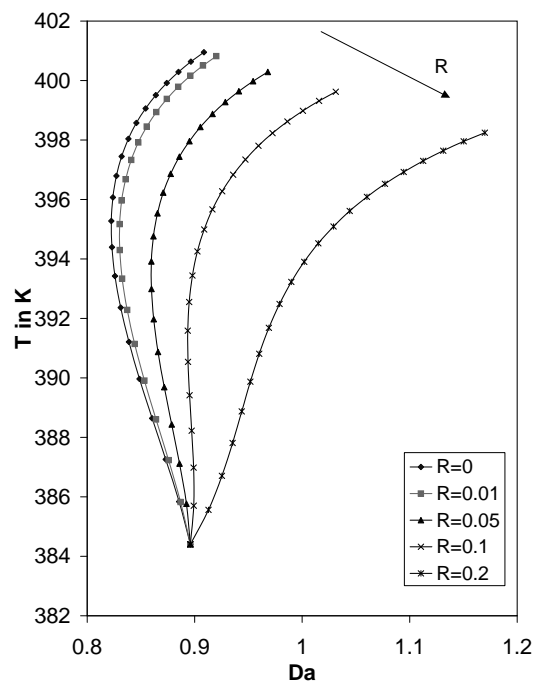
**Figure 4:** The presence of a separation operation allows the system to display output multiplicity as a reactive flash.

the system, as both  $T$  and  $x$  increase simultaneously. This increase in reaction rate can promote the appearance of steady state multiplicity in the system. Therefore the fact that one is carrying out a separation and reaction simultaneously can lead to the appearance of multiple steady states even for some cases in which a single steady state is observed for every  $Da$  for the one phase CSTR.

Figure 4 presents the results for a system that does not display multiple steady states as a one phase CSTR but does as a reactive flash. One can observe the locus of steady states for the one phase CSTR in the figure and the fact that there is a single steady state for each value of  $Da$ . On the other hand, as the pressure is decreased and the system is allowed to reach a boiling point one can notice the appearance of two steady states for different values of  $Da$  within the two phase region. As before the two phase region starts at  $\phi = 0$  and ends at  $\phi = 1$ .

### Flash and Condenser

The influence of heat removal on the behavior of the system can be studied with the addition of a condenser to the vapor stream leaving the reactive flash. A reboiler or heating the flash directly would be necessary if the heat of reaction was not large enough to boil the reacting mixture (since enough heat is provided by the heat of reaction, external heating is not included in this

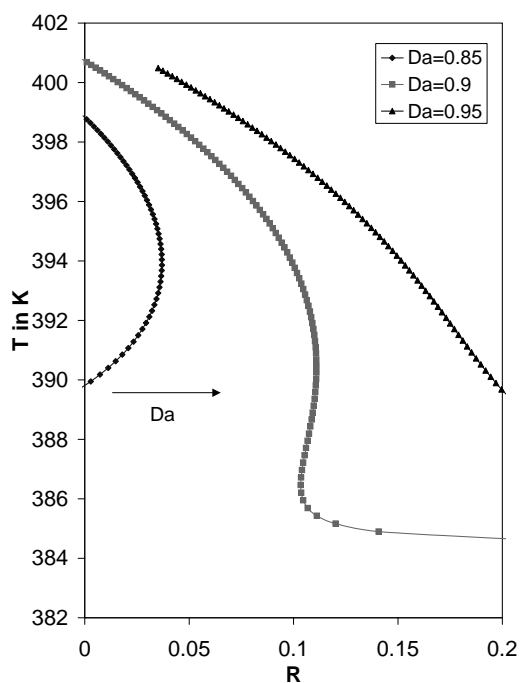


**Figure 5:** As the reflux ratio  $R$  increases, the region of multiplicity decreases and eventually only one steady state exists for the reactive flash with condenser.

analysis). The total condenser provides saturated liquid product and reflux but no chemical reaction. The exiting saturated liquid from this unit is partly removed as distillate and the rest returned as reflux to the reactive flash.

One could use this heat removal unit to possibly remove the steady state multiplicity observed in the cases when  $\Lambda < 0$ . The following figures show the results for a system in which the value of  $\Lambda$  is negative at zero reflux. When the reflux is equal to zero, this system corresponds to a reactive flash with  $\Lambda < 0$ , similar to the ones presented earlier.

In Figure 5, adding a condenser to the system can reduce the region of multiplicity until one is left with a single steady state for each value of  $Da$ . The addition of this condenser has more than one effect on the system. It removes energy released by reaction and lowers the temperature of the flash by introducing a cooler stream. For the reactive flash examples discussed previously, multiplicity exists as the separation in the system improves and the reaction is enhanced by the increase in temperature as well as reactant concentration. By returning this colder stream which has a larger concentration of product than the reacting mixture does, one reduces the enhancing effect that the separation has on the reaction (and the heat generated by it). Ultimately this causes the reduction and eventual elimination of the multiple



**Figure 6:** There is output multiplicity for some values of the reflux ratio  $R$ .

steady states for the reactive flash/condenser system.

Figure 6 depicts the situation for which we already have a fixed  $Da$  and would like to affect the purity or conversion by adjusting the reflux ratio,  $R$ . Once again, at high  $R$  there is a single steady state. At lower values of the Damköhler number there are two and sometimes three steady states possible for certain  $R$  values. At  $R = 0$  the model reduces to that of the reactive flash where there were only two steady states for the particular  $Da$  chosen ( $Da = 0.85$ ), for example. As  $Da$  increases the region of output multiplicity decreases and eventually only a single steady state is possible for each value of  $R$ .

## Conclusion

The presence of vapor-liquid separation can remove or promote the appearance of multiple steady states in a reactive flash operated adiabatically and isobarically. Under some reasonable assumptions, the quantity  $\Lambda$ , relating the heat of vaporization, heat of reaction and the compositions in the system, is shown to be a key quantity to determine when steady state multiplicity is possible for the system. A negative value of  $\Lambda$  allows the system to operate in a region where the rate of reaction is enhanced by an increase in temperature as well as reactant composition in the liquid phase. In considering both the CSTR one phase steady states and the reactive flash, input and output multiplicities can be observed in some systems.

The use of a heat transfer unit for removing heat can reduce the region of instability and eventually eliminate steady state multiplicity. This could be accomplished by adding a total condenser to the vapor stream effluent from the reactive flash. As the reflux increases, the steady state multiplicities eventually disappear.

## Acknowledgments

We gratefully acknowledge financial support from the sponsors of the Process Design and Control Center, University of Massachusetts-Amherst and from the donors of the Petroleum Research Fund, administered by the American Chemical Society (grants ACS-PRF #35612-AC9 and ACS-PRF #32221-G9).

## References

- Alejski, K. and F. Duprat, "Dynamic simulation of the multicomponent reactive distillation," *Chem. Eng. Sci.*, **51**, 4237 (1996).
- An, X. W. and Y. D. Xie, "Enthalpy of isomerization of quadricyclane to norbornadiene," *Thermochimica Acta*, **220**, 17 (1993).
- Ciric, A. R. and P. Miao, "Steady state multiplicities in an ethylene glycol reactive distillation column," *Ind. Eng. Chem. Res.*, **33**, 2738 (1994).
- Damköhler, G., "Stromungs- und wärmeübergangsprobleme in chemischer technick und forschung," *Die Chemische Fabrik*, **12**, 469 (1939).
- Doherty, M. F. and M. F. Malone, *Conceptual Design of Distillation Systems*. McGraw-Hill, New York (2001).
- Frenkel, M. L., G. Y. Kabo, and G. N. Roganov, *Thermodynamic Properties of Isomerization Reactions*. Hemisphere Publishing Corporation, Washington, DC (1993).
- Grosser, J. H., M. F. Doherty, and M. F. Malone, "Modeling of reactive distillation systems," *Ind. Eng. Chem. Res.*, **26**, 983 (1987).
- Güttinger, T. E. and M. Morari, "Predicting multiple steady states in equilibrium reactive distillation. 1. Analysis of nonhybrid systems," *Ind. Eng. Chem. Res.*, **38**, 1633 (1999).
- Hauan, S., T. Hertzberg, and K. M. Lien, "Multiplicity in reactive distillation of MTBE," *Comput. Chem. Eng.*, **21**, 1117 (1997).
- Kumar, A. and P. Daoutidis, "Modeling, analysis and control of ethylene glycol reactive distillation column," *AIChE J.*, **45**, 51 (1999).
- Rodríguez, I. E., A. Zheng, and M. F. Malone, "The stability of a reactive flash," *Chem. Eng. Sci.*, **56**, 4737 (2001).