On the Multiple Solutions of the Reactive Distillation Column for Production of Fuel Ethers

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A systematic study of the operating conditions and parameter sensibility of multiple steady states in a reactive distillation column for production of fuel ethers is presented. The multiplicity analysis is performed using bifurcation diagrams for several scenarios using the process simulator Aspen One Aspen Plus. Our results indicate that the main variables that affect both the presence and behavior of multiple solutions in the reactive distillation column are the reflux ratio, the reboiler duty and the thermal condition in the feed stream. In particular, we have determined that the vapor-liquid stream in the feed has a major influence on the occurrence of this phenomenon and this parameter especially establishes the type of multiplicity that can occur in the reactive distillation column for production of fuel ethers.

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1. Introduction

In chemical process industries, chemical reaction and purification of the desired products by distillation are usually carried out sequentially. In several cases, the performance of this classic chemical process structure can be significantly improved by integration of reaction and separation in a single multifunctional process unit. This integration concept is called ‘reactive distillation’ (RD). Thus, reactive distillation combines a chemical reactor and a distillation column in a single unit operation. By performing reaction and separation simultaneously, chemical equilibrium can be shifted toward maximum conversion. Economic benefits also result from direct heat integration and reduction of equipment costs [1,2]. Reactive distillation has been employed in industry for decades, but it has received renewed attention in recent years. Because of the potential advantages of this technology including its improvements in terms of capital, productivity and selectivity, reduced energy use, and reduction or elimination of solvents; the study of this separation scheme has increased significantly and several techniques for designing reactive distillation columns have been proposed in the past decade (e.g., [3–8]). Overall, the design of reactive distillation columns is more complex than its nonreactive counterpart due to the nonlinear behavior of process models and the simultaneous presence of physical and chemical equilibrium. These characteristics may cause the presence of solution multiplicity during the design and modeling of reactive separation schemes.

The importance of multiplicity of solutions in separation processes relies on the fact that one set of design parameters can yield several operating conditions. A consequence of this situation is that control actions must be taken to regulate the process operation [9]. In process system engineering, it is important to predict all multiple states, within the practical domain of operating variables, to know whether they are desirable, and to understand how the separation scheme and its performance response to changes in the operating conditions. Multiplicity of solutions in separation processes has been a largely studied problem. While some results state the uniqueness of solution for binary distillation, other studies have concluded that multiple steady state can arise in binary distillation if the flow rates are given on a mass basis instead of a molar basis, or if multicomponent mixtures are separated in processes with an increase of the number of stages [10,11]. Regarding reactive distillation, several works have reported the existence of multiple steady states in both theoretical and experimental studies (e.g., [10,12–16]). Some authors have studied and analyzed the presence of multiplicity in reactive distillation columns using several operative variables and design parameters such as the system configuration, the selection of both thermodynamic and kinetic models, the reflux ratio, and the location of feed inlets, among others [17]. It is important to remark that the existence and
possible explanation of multiplicity in reactive distillation columns have been investigated by several authors for well-known reactive systems [18].

Despite the large amount of reported results on multiplicity in reactive distillation, only some papers have been discussed their causes and implications for operation and control of these separations schemes (e.g., [19–21]). For example, one of the first systematic approaches to the problem of controlling reactive distillation was addressed by Kumar and Daoutidis [22]. The main control objective is to control the product purity using the reboiler heat input. As a preliminary study, a bifurcation analysis was performed, which revealed a region of output multiplicity and a transition from minimum-phase behavior at moderate product purity to a nonminimum-phase behavior at high product purity. For the case of an ethylene glycol reactive distillation column, a nonlinear controller was designed that yields good performance in setpoint tracking.

According to literature, reactive separation systems can exhibit two types of multiplicity: input and output multiplicity [23]. Input multiplicity occurs when two or more sets of input variables produce the same output conditions, while output multiplicity occurs when one set of input variables results in two or more independent sets of output variables [23]; Fig. 1 illustrates these types of multiplicity. It is convenient to remark that the input variables of separation processes are those that can be manipulated by controllers. These variables include the reflux ratio, reboiler duty, and feed flow, among others. On the other hand, the output variables can be also controlled or used to describe the process conditions, e.g., the stage temperatures and compositions [24]. Both input and output multiplicities are relevant and important because of they may impose control and operation problems [25–27]. In particular, Kumar and Kaistha [27] have analyzed the control implications of both input and output multiplicity in the design of a reactive distillation column. For example, the control of systems with input multiplicity using conventional controllers (i.e., PI or integral controller) may face operating problems such as the driving of the system to a lesser stable input steady-state or to a lesser economical steady-state or even yielding unconstrained limit cycles [25]. With respect to the output multiplicity, the output of the system for a particular value of input depends on the process history and, consequently, the characteristics of the system could be different for the same input. Therefore, the controlled system can respond differently to similar changes in manipulation depending on the history of the system [25]. It is convenient to remark that the presence of input and output multiplicities is caused by the nonlinearity of the system [24,27]. So, these multiple solutions can be eliminated by placing constraints on the manipulated variables, by increasing the number of controlled variables and by a proper choice of the operating policy of the system, i.e., the selection of controlled variables [25,27]. In summary, the presence of both types of multiplicity in reactive distillation columns is possible; or even the presence of a combination of them may also occur [16]. This combination of different multiple states is known as input–output multiplicity or multiplicity of internal states where multiple groups of internal conditions or profiles are localized to the same values of input and output variables. Fig. 1c illustrates the input–output multiplicity. To the best of author’s knowledge, the study of this hybrid multiplicity has not been extensively studied in the available literature of reactive separation schemes.

In this study, we have predicted the existence of input and input–output multiplicities in reactive distillation separations for fuel ethers: MTBE (methyl tert-butyl ether) and TAME (tert-amyl methyl ether). Multiplicity analysis was performed using the commercial simulator Aspen One Aspen Plus. We have obtained bifurcation diagrams showing the presence and type of multiplicity in these reactive systems considered as cases of study. We also studied the effect of the vapor–liquid mixture of the feed streams on the presence of multiple solutions, which is a parameter that had not been considered in the multiplicity analysis, despite it is closely related to the design and operating costs of any separation system either nonreactive or reactive. Therefore, this study provides new insights on the multiplicity of solutions in reactive distillation columns.

2. Statement of the problem of multiple states in a reactive distillation column

In the first instance, we have considered the schematic configuration of a distillation column shown in Fig. 2. In this diagram,
the use of distillation lines, the material balance can be presented and solved algebraically starting from the limits of the column (top and bottom) and setting a given composition of column product.

As stated by other authors (e.g. [16]), the usage of simulators does not directly provide results indicating the presence of multiple stationary states because of they are designed to obtain a unique solution. The identification of additional solutions can be performed using a sensitivity analysis on the system in one or more operation parameters or by varying the initial estimates of the previous solution [16]. In general, the construction of bifurcation diagrams using modular simulators is not straightforward; this is due to the traditional numerical algorithms, which are used and incorporated into commercial process simulators for solving nonlinear equation systems, usually converge to one solution only. So, these additional steady state solutions may be found by defining the operating conditions of the case of study, and performing a sensitivity analysis on one or more parameters, or varying the initial guesses of the previous solution [16]. It should be understood that, in this case, by sensitivity analysis, we mean the study of the effect of changes in input variables on the process (i.e., model) outputs. On the other hand, it is convenient to note that a bifurcation is a fundamental change in the nature of a solution and, as a consequence, bifurcation diagrams can be used for detecting the presence of solution multiplicity in separation processes. Specifically, this approach for multiplicity analysis can be performed in ASPEN PLUS via the following four steps [16]: (i) specification of measured variable; (ii) specification of manipulated variable; (iii) specification of the range of analysis for the manipulated variable; and (iv) specification of the quantities to be calculated and analyzed. So, we have used this basic and reliable methodology for tracking multiple steady states of the reactive distillation columns for production of fuel ethers in ASPEN PLUS.

Reactive distillation columns were simulated using the RADFRAC module of ASPEN PLUS, where the following specifications were required for modeling the reactive distillation column: components, feed conditions, operating pressure, property model, column configuration (feed stage location, number of stages, reactive stages, holdups, type of condenser and reboiler), two operating specifications (in this case, reflux ratio and distillate flowrate), and the reaction type. It is important to highlight that preliminary designs of reactive columns (i.e., number of stages, feed stage, reflux ratio) were obtained using the methodology proposed by Carrera-Rodriguez et al. [8]. Tables 1 and 2 show the molar compositions of the components for the production of MTBE and TAME for each of the thermal conditions of the feed analyzed in this multiplicity study. Table 3 provides information on the configuration of the reactive columns derived from the methodology of Carrera-Rodriguez et al. [8]. Once defined the configurations of the reactive columns, they were simulated in Aspen Plus to detect the presence of multiple steady states following the approach described by Cardenas-Guerra et al. [16].

To perform the corresponding simulations, other specific aspects of the column configuration were defined. Table 4 shows the configuration characteristics of the cases of study, which were considered valid for both systems regardless of type of feed stream.

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**Table 1**

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Feed thermal condition (ψ)</th>
<th>Feed composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Isobutene</td>
</tr>
<tr>
<td>A1 + A2 ↔ A3, and A4 as inert</td>
<td>0</td>
<td>0.329342</td>
</tr>
<tr>
<td>(1) Isobutene</td>
<td>0.25</td>
<td>0.329342</td>
</tr>
<tr>
<td>(2) Methanol</td>
<td>0.5</td>
<td>0.298059</td>
</tr>
<tr>
<td>(3) MTBE</td>
<td>0.666</td>
<td>0.329342</td>
</tr>
<tr>
<td>(4) n-Butane</td>
<td>1.0</td>
<td>0.31345</td>
</tr>
</tbody>
</table>

---

**Fig. 2.** Schematic diagram of the configuration of a distillation column.
Wilson local composition model was used as thermodynamic model for the calculations of phase equilibrium (liquid–vapor) in both systems. However, in the column design and the corresponding process simulation, we do not use the Wilson parameter values stored in database of ASPEN PLUS. In particular, Tables 5 and 6 show the values of the interaction parameters for Wilson model used in the simulations of the systems MTBE and TAME, respectively. An equilibrium model has been used for the simulation of the reactive distillation columns [8].

For the MTBE and TAME cases the equilibrium constants can be determined using Eqs. (1) and (2), respectively.

\[
\ln K_{eq} = -10.0982 + \frac{4205.05}{T} + 0.2667 \ln T \quad (1)
\]

\[
\ln K_{eq} = -9.1549 + \frac{4273.5}{T} \quad (2)
\]

with \( T \) in K.

This model assumes that the system is at the thermodynamic equilibrium and, consequently, it is simpler and requires a lower number of model parameters for performing a conceptual analysis of multiple solutions in reactive separation schemes [2,28,29]. Therefore, this approach using equilibrium model provides an initial perspective for multiplicity analysis and can be considered as a limiting case for the prediction of multiple solutions in reactive distillation columns using the tested design variables and cases of study. Finally, the reboiler duty was considered as the parameter of continuity, whereas only the reflux ratio was studied to measure their effect on the presence or absence of multiplicity. Thus, the reboiler duty was varied within a certain operating range while the reflux ratio was maintained fixed at a given value. Under this approach, simulations were performed for the two reactive systems at different operating conditions.

### 3. Results

The results for each of these cases of study are described in the following sections.
3.1. Multiplicity in the reactive system for the production of MTBE

As already mentioned, the sensitivity analysis was performed using the reboiler duty as the main sensitivity variable in a defined range between 10 and 300 kW. This analysis was performed at various reflux ratios, between 1 and 6, to study the effect of this variable on the presence or absence of multiplicity. It should be noted that in the calculations made for the sensitivity analysis, the above parameters are considered as independent variables and the mole fraction of the product was considered as the dependent variable, where the molar fraction diagrams were used to identify the presence of the multiple states via bifurcations. However, for practical purposes, the composition of the main component of the reaction has been considered only in this study, which corresponds to the product of interest of each reactive system, being the MTBE for this example. This component is obtained as the distillate and in the bottoms of the column as a product. However, this also corresponds to the less volatile component (heavier component) and, as a result, it is obtained in higher proportions in the column bottoms in comparison to the distillate. Fig. 3 shows the response surfaces of the composition of MTBE in the bottoms of the column obtained from the sensitivity analysis for different reflux conditions and considering the different thermal conditions in the feed stream. Bifurcation diagrams indicate that in all cases there is the presence of multiple stationary states of input type. These results are in agreement with those reported by [15,18,30]. Specifically, Jacobs and Krishna [30] and Chen et al. [15] have reported that the presence of multiple solutions for MTBE reactive distillation column is feasible for operating conditions that approach the thermodynamic equilibrium. In fact, we can observe that the behavior that presents the molar fraction of MTBE is concave with respect to the reboiler heat load. Also, these results show how the concavity, which indicates the presence of multiplicity, is accentuated at low reflux ratios and, if this parameter increases, the multiplicity is gradually disappearing. In particular, Eldarsi and Douglas [31] and Chen et al. [15] have also reported that the ranges of reflux ratio for multiple solutions are sensitive to the column operating conditions for MTBE synthesis. Note that the reflux ratio affects the process performance because it has a significant impact on the separation capability of the reactive distillation column and, consequently, it is an indirect variable to study the effects of the vapor and liquid flows on the presence of multiple solutions. Table 7 shows the reflux ratio ranges where the presence of input multiplicity prevails for each of the thermal condition of the feed stream studied. Overall, the presence of multiplicity significantly depends on the feed thermal condition and it appears that the presence of multiple solutions for MTBE composition decreases with respect to \( \psi \). This implies that the input multiplicity for MTBE composition is more significant if a saturated liquid is the feed of the reactive distillation column. This result has implications for the selection of the operating conditions of the reactive distillation column.

3.2. Multiplicity in the reactive system for the production of TAME

Similar to the previous system, the sensitivity analysis was performed using the reboiler duty as continuity variable in a study range from 1 to 1500 kW. In addition, we have analyzed different conditions of reflux in the reactive column from 1 to 8 to study the effect of such parameters on the presence of multiple solutions. In particular, this system has major implications in terms of multiple solutions compared to the system for the production of MTBE. Bifurcation diagrams were obtained considering the TAME composition in the bottom of the column because this is the compound of interest of that reaction. In addition, TAME is the least volatile component of the system and is obtained at higher composition in the bottoms of the column. Fig. 4 shows the response surfaces obtained for the TAME composition in the bottoms of the column for different thermal conditions of the feed stream and the studied reflux ratios. Results obtained in this study indicate that regardless of the thermal condition in the feed stream, the presence of multiple solutions is present in all cases. Thus, the predominant type of multiplicity is input (i.e., concave behavior of TAME composition) with respect to reboiler duty. These results also show how this concave behavior becomes more pronounced for low reflux ratios. Note that Mohl et al. [18] have reported the presence of multiplicity in TAME system at low reflux ratios. Additionally, in some cases, as the reflux ratio is increasing, this type of behavior is gradually removed, and especially for some conditions of reflux, the surface response is no longer continuous. This discontinuity is an indication of the presence of type of output or input–output
multiplicity. In fact, simulation results indicate the presence of different-type multiple states for a given operating region. Based on the results, Table 8 reports the reflux ratio ranges where the multiplicity, including its type: input or input–output, occurs for each of the thermal conditions studied for the feed stream. Overall, the input multiplicity is present for all thermal conditions of the feed stream inside the studied range of the reflux ratio. Reflux ratio and reboiler duty are design variables that determine the temperature and composition profiles obtained from the simultaneous physical and chemical equilibrium inside the reactive distillation
column. As expected, they have a significant impact on the complex interactions between the reaction and separation and may induce the presence of multiple solutions in reactive distillation columns. Note that output multiplicity was not observed in this reactive system. Furthermore, the input–output multiplicity is presented for some operating conditions and for certain regions of the reflux ratio. Specifically, these conditions correspond to those columns with: (1) a saturated liquid feed stream and (2) a feed stream with a vapor–liquid ratio of 0.75. For illustrative purposes, Fig. 5 clearly identifies the region where this multiplicity occurs, which

Fig. 4. Composition of TAME in the bottoms of reactive distillation column as a function of reboiler duty and the reflux ratio. Feed stream with a thermal condition of: (a) $\psi = 0$, (b) $\psi = 0.25$, (c) $\psi = 0.5$, (d) $\psi = 0.75$ and (e) $\psi = 1.0$. 
Table 8
Operating ranges for the reflux ratio where there are multiple solutions to the different thermal conditions of feed stream to the reactive system for the production of TAME.

<table>
<thead>
<tr>
<th>Thermal condition (ψ)</th>
<th>Range of reflux where the multiplicity of solutions can occur</th>
<th>Input multiplicity</th>
<th>Output multiplicity</th>
<th>Input–output multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>≤[1,8]</td>
<td>–</td>
<td>–</td>
<td>≤[&gt;4,8]</td>
</tr>
<tr>
<td>0.25</td>
<td>≤[1,8]</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.5</td>
<td>≤[1,8]</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.75</td>
<td>≤[1,8]</td>
<td>–</td>
<td>–</td>
<td>≤[&gt;7.5,8]</td>
</tr>
<tr>
<td>1</td>
<td>≤[1,8]</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

is limited by two points. Note that these points are obtained in the sensitivity analysis via increments and decrements of the reboiler duty. Specifically, when the reboiler duty gradually increases from 15 to 1500 kW, one of the return points is detected at 571.35 kW; while the other discontinuity point is identified at 561.31 kW via the gradual decrement of the reboiler duty from 1500 to 15 kW. Both points define the region of multiplicity and are located at the boundaries of the curves of the upper and lower steady state, respectively. Also it should be noted that there are three points located within the region and which may indicates the presence of multiplicity output: two of them form the limits of lower and upper curve stable state and a third point located in the region of the intermediate curve. However, since this intermediate curve is not easily identifiable due to the unstable behavior of the simulator and, because of it also has no practical significance for the system (point of instability), this identification was not performed. For practical purposes, it is more useful to identify the area of multiplicity and the points that surround it (i.e., lower and upper curves) due to they represent solutions that are considered stable, which means being solutions with a practical significance for the studied system [16].

Finally, it is convenient to remark that previous studies have reported the presence of multiple solutions for the TAME process if the reactive distillation column is operated especially in the kinetic regime of the reaction (e.g., [15,18]). In fact, these studies concluded that multiple solutions of TAME process are more sensitive to the effects of reaction kinetics and the multiplicities disappear as the system approaches the thermodynamic equilibrium. The prediction of multiple solutions in reactive distillation columns depends significantly on the column configuration (e.g., number of stages, feed location and composition), the quantity and the type of design and operating variables used in the multiplicity analysis besides to the thermodynamic data and models used for the simulation [27,29,32]. Based on these facts, the differences between the results of this study and those reported in literature are mainly caused by the design information used for the cases of study. Also, it is important to highlight that the profiles of composition, reaction and temperature are consistent with those reported in [8] (see Figs. 6–8 for the MTBE case, as a representative study).

As stated in literature, both equilibrium and nonequilibrium stage models can be used for the design of reactive distillation columns (RDC). Several studies have reported that both approaches have advantages and limitations for the modeling of RDC including the prediction of multiple solutions. In particular, the nonequilibrium stage model requires more detailed information of the system to be studied, which is used for the calculation of mass transfer coefficients, interfacial areas, liquid hold-ups and for determining the effect of nonideal component behavior on the calculation of reaction rates and chemical equilibrium constants [32]. These parameters of the nonequilibrium stage model may have a significant impact on the performance and design of reactive distillation columns [33]. For example, Švandová et al. [33] have concluded that the accuracy of the nonequilibrium stage model for the prediction

![Fig. 5](image_url)  
**Fig. 5.** Composition of TAME in the bottoms of the reactive distillation column as a function of reboiler duty for a thermal condition in the feed stream of ψ=0.
and design of RDC can be limited to the accuracy of the correlations used to estimate the mass transfer coefficients and interfacial area. In general, studies reported in the literature indicated that the window within which multiplicity of RDC is observed may be narrower with the nonequilibrium stage model in comparison to the equilibrium stage model (e.g., [29,32,33]). This implies that the results obtained with the equilibrium stage model can be considered as a limit case for the prediction and analysis of multiplicity in reactive distillation columns. Herein, it is convenient to note that the nonequilibrium stage model shows a higher nonlinear behavior than that of the equilibrium model and, as expected, numerical convergence problems can arise and a wrong initial guess for the design
variables may conduct to different design results [33]. In summary, some authors (e.g., [33]) have recognized that the description and prediction of RDC using a universal model is very challenging and, even using a rigorous model, there may be a lack of accurate estimations of all parameters of the model and, consequently, the modeling results of RDC depend strongly on the available information. Based on these facts, we have used an equilibrium stage model as an initial approach for predicting and analyzing the presence of multiple solutions on reactive distillation columns of selected cases of study and tested design variables. Therefore, the results obtained in this study can be used as initial estimate for multiplicity analysis in reactive distillation columns using a more rigorous modeling approach.

4. Conclusions

A systematic study has been performed of the operating conditions under which multiple solutions may occur in reactive distillation columns for production of TAME and MTBE. Multiplicity analysis was performed using the commercial simulator ASPEN PLUS and using the reboiler duty as sensitivity parameter, and the reflux ratio as comparative parameter. Both parameters are related to the proper design of this type of separation systems. Specifically, in this work bifurcation diagrams were developed, which show the presence and type of multiplicity in the systems considered as cases of study. Also, we have studied the effect of the vapor–liquid present in the feed streams on the presence of multiplicity, which is a parameter that to date had not been considered in this analysis despite it is closely related to the design and operation costs of any separation system with or with reactions. Thus, the results obtained in this study indicate that given the complexity and nonlinearity presented by reactive distillation columns is common the presence of the phenomenon of multiplicity, in particular the input multiplicity and in some cases the input–output multiplicity. Also, it shows the influence or effect of reflux ratio in the columns on the presence or absence of the phenomenon of multiplicity, where the phenomenon becomes more pronounced at low values and disappears as this parameter increases. Moreover, it indicates that the vapor–liquid stream in the feed has a major influence on the occurrence of this phenomenon and in particular about the kind of multiplicity that can occur in the reactive column. Based on the fact that the model complexity influences the identification and prediction of multiple states in reactive distillation columns, results of this study should be complemented using a more rigorous nonequilibrium model. This topic will be addressed in future studies of our research group.

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References


