AmbarPro

Advanced Modelling of Reactive Distillation Columns

Detecting and Managing Multiple Steady States

An AmbarPro Whitepaper on Custom Process Modelling and Simulation

Executive Summary

Reactive distillation (RD) is a mature process intensification technology that integrates chemical reaction and distillation within a single column, offering significant advantages in terms of conversion, energy efficiency, and equipment cost. However, the simultaneous occurrence of reaction and separation introduces strong nonlinearities and can lead to multiple steady states, complicating operation and control.

This whitepaper presents a detailed study of a monopropylene glycol (MPG) reactive distillation column, highlighting the challenges associated with steady-state multiplicity. Using custom first-principles modelling combined with homotopy continuation, all possible steady states were identified and characterized in terms of temperature and composition profiles across the column.

AmbarPro Modelling Approach

This whitepaper demonstrates AmbarPro's capability to develop fully custom, first-principles models of complex process units. By applying homotopy continuation methods to a reactive distillation column, AmbarPro identifies all possible steady states—including unstable and undesired operating regimes that standard simulations cannot detect. This insight enables safer operation, improved start-up procedures, robust control strategies, and operation closer to optimal economic performance.

Key Findings

- The system can exhibit low-, intermediate-, and high-productivity steady states, with the intermediate state typically unstable.
- Small perturbations in feed, temperature, or reflux can trigger transitions between states, affecting product yield and energy requirements.
- Appropriate control strategies, start-up procedures, and design adjustments—such as feed distribution, reboiler duty, and reaction volume—are essential to ensure stable, high-conversion operation.
- Custom modelling enables predictive insight into column behaviour, supporting safer operation, robust control, and optimized process performance.

Introduction & Background

In industrial practice, process intensification technologies are often regarded as high-risk despite their potential benefits in terms of energy efficiency, CAPEX and OPEX reduction, lower consumption of auxiliary chemicals, and land footprint minimization [1,2]. This hesitation is not driven by a lack of theoretical understanding, but by the operational complexity and strong nonlinear behaviour that intensified units can exhibit once deployed at scale.

Among the different intensified technologies, reactive distillation (RD) columns are one of the most mature and widely applied. An RD column integrates chemical reaction and distillation in a single apparatus. Structurally, it resembles a conventional distillation tower equipped with trays, but with the key difference that the liquid phase contains an active catalyst—either on specific trays or distributed across the entire column (Figure 1). The simultaneous occurrence of reaction and separation enables reaction equilibrium to be shifted through continuous product removal, while allowing reaction heat to be directly integrated into the separation process. From an operational perspective, the tight coupling between reaction, separation, and energy balance makes reactive distillation columns particularly sensitive to disturbances and initialization conditions.

This integration offers several well-known advantages compared to conventional reactor–separator configurations:

- Higher conversion: Continuous removal of products from the reactive zone shifts equilibrium toward products (Le Chatelier's principle), which is especially beneficial for equilibrium-limited reactions.
- Reduced capital investment: A single RD unit can replace multiple standalone operations such as a reactor, a heat exchanger, flash vessels, and a distillation column.
- Energy savings: The heat released by the reaction can be directly used to drive separation, improving thermal integration.
- Lower solvent consumption: Additional extraction or reaction solvents can often be eliminated.
- Fewer side reactions: Immediate removal of products reduces their exposure to reactive conditions, suppressing undesired secondary reactions and thus, undesired byproducts.

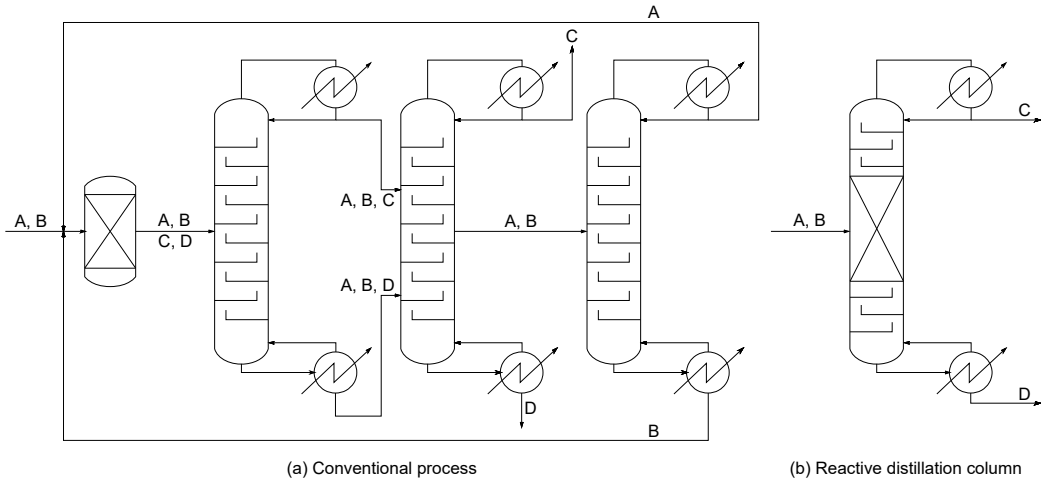

Figure 1. Processing schemes for the reaction A + B ⇌ C + D, where C and D are both desired products. (a) Typical conventional process configuration consisting of a reactor followed by a distillation train. (b) Reactive distillation configuration. Components A, C, D, and B are arranged in order of increasing boiling point. Adapted from [3]

Problem Statement & Technical Challenges

Despite their numerous advantages, reactive distillation columns also present important operational challenges. Due to the fact that reaction and separation occur simultaneously in the same unit, the internal dynamics of the column are strongly coupled. As a result, the control of an RD column becomes more challenging compared to having both processes in separate reactor and distillation units.

These strong nonlinearities can lead to the existence of multiple steady states, under which identical nominal operating conditions result in fundamentally different internal column behaviours and product outcomes.

Steady-state multiplicity and operational risk

A particularly critical issue found in some RD systems is the presence of multiple steady states. Under certain operating conditions, an RD column can exhibit steady-state multiplicity: identical inputs—feed flow rates and compositions, reboiler and condenser duties, reflux ratio, and pressure—may lead to different internal operating states once steady conditions are reached. Consequently, the product compositions at the outlet streams can change significantly even when the inputs remain constant.

This is problematic for two reasons:

1. Only one of the steady states may deliver the desired product quality and yield, while others can lead to off-spec material or excessive byproduct formation.
2. Some steady states may be unstable, meaning that small disturbances can push the system toward a different operating regime, complicating process control and potentially compromising the column performance.

Industrial case study: monopropylene glycol production

To investigate these phenomena in an industrially relevant context, a detailed case study was carried out by AmbarPro on a reactive distillation column used for the production of monopropylene glycol (MPG). MPG ($C_2H_8O_2$) is a widely used compound in industries such as antifreeze formulations, resins, cosmetics, and pharmaceuticals. It is traditionally synthesized via the hydration of propylene oxide (PO), a reaction that also generates two undesired byproducts: dipropylene glycol (DPG) and tripropylene glycol (TPG). The reactions happening in the reactor are the following:

$$OP + H_2O \xrightarrow{k_1} MPG$$

$$OP + MPG \xrightarrow{k_2} DPG$$

$$OP + DPG \xrightarrow{k_3} TPG$$

In the conventional production route, unreacted species are recovered through a series of evaporators and flash vessels and recycled back to the reactor. MPG is then separated from the heavier glycols through a multi-column distillation train.

In contrast, the RD process performs all steps within a single column, leveraging reaction heat to enhance MPG selectivity. The studied column operates at 11 bar(a) and contains 16 trays. Water

(5,760 kg/h) is fed on the first tray, while PO (9,000 kg/h) is injected on tray 10 (Figure 2). The system operates under total reflux, meaning no overhead product is withdrawn, with a total reboiler duty of 23 MW. The catalyst is uniformly distributed throughout the column, enabling reaction in every liquid-containing stage, including the reboiler and the condenser.

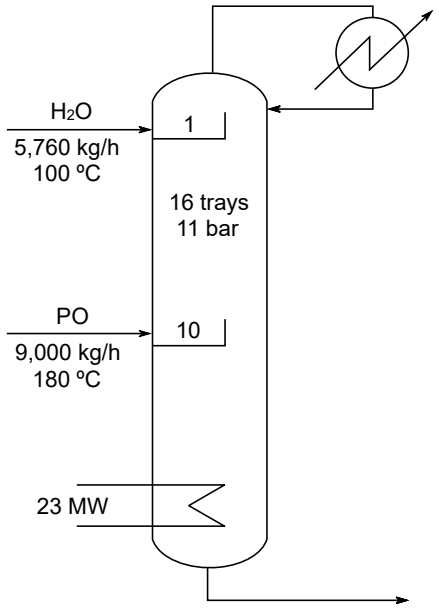

Figure 2. Schematic representation of the reactive distillation (RD) column configuration for MPG synthesis

Modelling and Numerical Framework for Detecting Multiple Steady States

Traditional algorithms used to find the steady state solutions, like the Naphtali-Sandholm method [4] and the inside-out method [5], are not designed to find multiple steady states. Depending on the initial values provided to the method to start the calculations, the algorithms may fail to converge to any solution due to the high nonlinearity governing the system. When convergence is achieved, the only way to detect multiple steady states is to vary the initial values of the variables, so that at some point this change leads to a different steady state from the previous one. However, this trial-and-error approach is inefficient and it often fails to find all the steady states, as they are discovered by probing the space of initial guesses. As a result, standard steady-state simulation workflows provide limited insight into the full range of feasible operating regimes. For this reason, numerical techniques capable of systematically exploring all solutions of a nonlinear system are preferred.

One of the most powerful of these techniques is homotopy continuation, which enables the identification of all steady-state solutions connected through a homotopy path [6,7]. Homotopic continuation is a numerical method that allows to find all the solutions connected among themselves via a homotopy. This method makes use of a known solution to find the others by varying the so named homotopic parameter.

Homotopy continuation constructs a continuous transformation between two systems:

- a simple auxiliary system $g(x)=0$ with a known unique solution, and
- the original nonlinear system $f(x)=0$ whose solutions are sought.

A linear homotopy is defined as:

$$H(x,\lambda)=\lambda\cdot f(x)+(1-\lambda)\cdot g(x)=0$$

where λ is the homotopy parameter. When $\lambda=0$, the solution of the homotopy corresponds to the unique solution of $g(x)=0$. The solutions of $f(x)=0$ correspond to the solutions of the homotopy when $\lambda=1$. Consequently, there exists a path between the single solution of $g(x)=0$ and the solutions of $f(x)=0$. All solutions of the homotopy equation $H(x,\lambda)=0$ define a homotopy curve in the (x,λ) space. The multiple solutions of the equation $f(x)=0$ are detected when the homotopy curve reaches a turning point (where its direction reverses) and crosses the line $\lambda=1$ more than once.

This formulation allows the solver to start from a non-reactive steady state that is easy to compute and then continuously deform the system until the actual reactive steady states—and their multiplicities—are reached.

The homotopic continuation is applied in the problem of the MPG reactive distillation column. Since it is relatively easy to find a solution of the system without reaction, the homotopic parameter is defined as the normalized reaction volume in each tray (the normalisation is done using the actual reaction volume). In that way, $g(x)$ becomes the set of equations of the column without any reaction volume $(\lambda=0)$, and $f(x)$ becomes the same set of equations with reaction $(\lambda=1)$.

The reactive distillation column model was developed by integrating kinetic equations, liquid-vapour equilibrium equations, and heat- and mass-balances equations across all 16 trays, including the reboiler and condenser. The complete model consists of several hundred coupled nonlinear algebraic equations solved simultaneously at steady state. The following representative equation is included to illustrate the mathematical complexity of the underlying model and the type of nonlinear relationships that govern the system's behaviour:

$$\psi_k\left(F_k+\frac{(1-\psi_{k-1})}{\psi_{k-1}}V_{k-1}+V_{k+1}+R_k\right)-V_k=0$$

To implement the homotopic continuation approach, the model of the column was developed and implemented in Matlab. The homotopy continuation approach was first implemented using CL MatCont (a continuation and bifurcation analysis toolbox for MATLAB) to benchmark and validate the behavior of reactive distillation columns exhibiting multiple steady states.

Subsequently, a custom proprietary implementation is utilized to allow full integration with the simulation framework and greater flexibility in solver selection, parameter control and model customization.

In addition to the implementation of the homotopy continuation method, property calculations were handled through two complementary approaches. First, custom property correlations were implemented directly within the in-house simulation framework, allowing full control and

transparency over the thermodynamic formulation. Second, Aspen Properties was dynamically linked via Excel through ActiveX automation, enabling rapid evaluation of physical and thermodynamic properties under varying process conditions. This hybrid strategy combines the reliability of industry-standard property databases with the flexibility required for advanced numerical analysis. The interaction between the different software environments is illustrated in Figure 3, which shows the data exchange and automation workflow between Matlab/CL MatCont, Excel, and Aspen Properties. This modelling architecture is part of AmbarPro's custom simulation framework and is used to support advanced analysis of highly nonlinear process units.

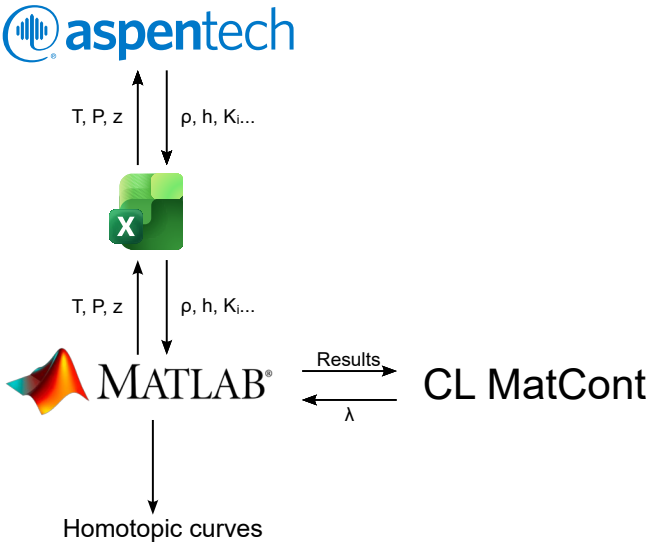

Figure 3. Data Exchange and automation architecture linking the different software environments

Results

With a fixed total inlet mass flow rate and total reflux at the top of the column, the outlet mass flow rate is the same. Thus, the most representative value of the column is provided by the molar flow rate of MPG at the column outlet. Figure 4 shows the homotopic curve of the molar flow rate of MPG at the column bottom as a function of the reaction volume in each tray, which is directly proportional to the homotopic parameter λ.

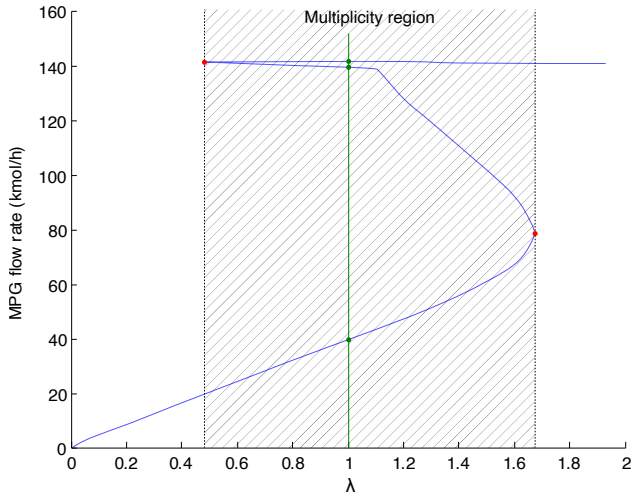

Figure 4. Homotopy curve of MPG bottom molar flow rate as a function of reaction volume

The system displays a high nonlinearity behaviour; this is the result of combining a reactive system in the liquid phase, the associated heat of reaction, a non-ideal vapour-liquid equilibrium and mass transfer between phases. In the design case, i.e., when $\lambda = 1$, there are three steady states. Unlike for ethlyene glycol reactive distillation columns [8], there are no small-scale multiplicities. The occurrence of the three steady states only happens when λ is between 0.4819 and 1.673. When 3 steady states could be present, typically the intermediate one is unstable and the lower and upper ones are stable, i.e., if the intermediate steady state is reached, any minimal change in the internal conditions of the column will enable the transition towards one of the other two stable steady states.

It is particularly relevant to compare the internal conditions of the column in terms of temperature and composition in the liquid phase (Figure 5). At the low-productivity steady state, the column remains largely PO-rich, with approximately 90 mol% PO and 10 mol% water throughout most trays. The temperature profile is nearly uniform at around 400 K, and the reaction takes place only in the lowest trays, where temperatures gradually increase to 440 K in the reboiler. This configuration represents a kinetically limited regime where the availability of water in the reactive zone is insufficient, leading to poor conversion and minimal MPG formation. The column effectively behaves as a physical separator with limited reactive enhancement.

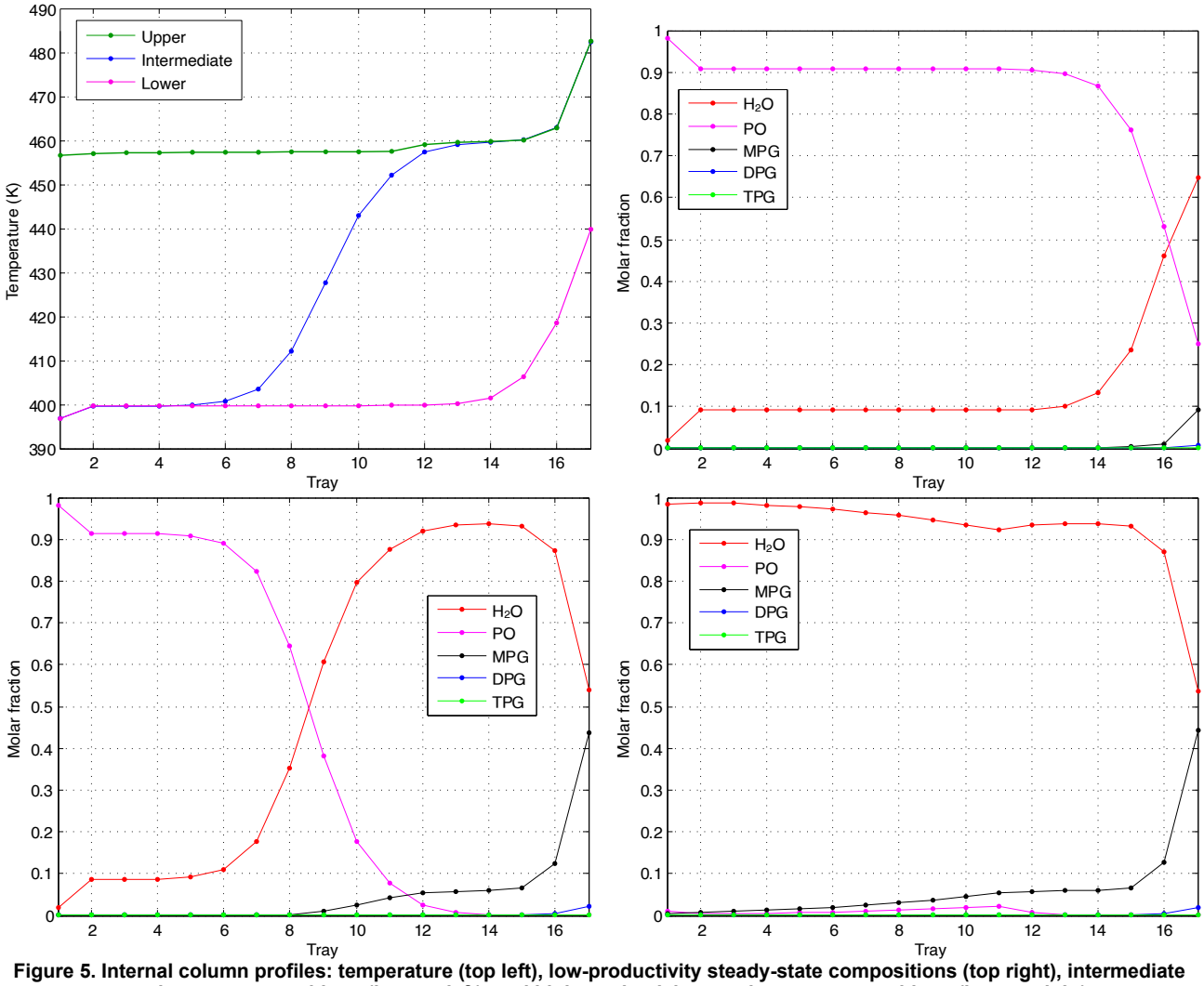

Figure 5. Internal column profiles: temperature (top left), low-productivity steady-state compositions (top right), intermediate steady-state compositions (bottom left), and high-productivity steady-state compositions (bottom right)

In the intermediate steady state, the upper part of the column (trays 1-8) behaves similarly to the low-productivity state ($\simeq$90 mol% PO, $\simeq$10 mol% water, $\simeq$400 K). However, below trays 8-9, a thermal and compositional front develops: temperature rises sharply to about 460 K, and the liquid composition reverses to 90-95 mol% water with almost no PO. This triggers significant MPG formation (around 5 mol%), driven by the strong exothermicity of the reaction. Near the bottom, water fraction decreases again, MPG concentration rises to about 40 mol%, and temperature reaches 483 K. This intermediate state reflects the coexistence of two reactive regimes—one PO-rich and one water-rich—separated by a reactive front that defines the column's thermal structure.

The high-productivity steady state corresponds to a water-dominated operation where nearly the entire column contains 92-98 mol% water and only traces of unreacted PO. The temperature remains constant at 457 K across most trays, indicating a self-sustained reactive zone, and then increases sharply to 483 K in the reboiler as the concentration of heavy glycols (MPG and DPG) rises. This state results from thermal feedback and mass-transfer coupling: once sufficient water reaches the reaction zone, the exothermic reaction accelerates, releasing more heat and shifting the vapour-liquid equilibrium to favour water condensation, reinforcing the high-conversion regime.

The intermediate steady state is most likely an unstable steady state, meaning that any little perturbation in the internal conditions of the column will shift it to the high-productivity steady state or to the low-productivity one. On the one hand, if the temperature in the upper trays slightly increases, the reaction between water and PO will be favoured, increasing even more the temperature due to its exothermicity, reaching eventually the high-productivity steady state. On the other hand, if the temperature in the lower trays decreases, the reaction that was happening at those trays will gradually slow down, providing less heat of reaction until the reaction almost stops, reaching the low-productivity steady state.

Small perturbations in feed composition, temperature, or reflux can move the column between these steady states, leading to drastic changes in product yield and energy profiles. Understanding these interactions is crucial for safe and efficient operation, as the system can exhibit hysteresis and sudden transitions between low- and high-conversion modes. Proper control of feed distribution, reboiler duty, and reflux ratio is therefore essential to maintain the desired reactive regime and ensure stable, high-quality glycol production.

Conclusion

Understanding the regions and operating conditions where multiple steady states occur in reactive distillation columns is essential for proper process design. This knowledge enables engineers either to prevent undesired states or to manage transitions toward the desired operating point.

This study has shown that a similar conversion could be achieved with reaction volumes of about 167% larger than those in the initial design, provided that hydraulic limitations and cost constraints are considered. Additionally, if the original design is to be implemented, the potential appearance of steady states different from the ones initially considered allows to know the conditions under which those occur, so that the control system of the reactive distillation column can be designed to handle the transition between them, either by increasing or decreasing the RD column internal temperature through the reboiler duty or by shifting the internal compositions by adjusting temporarily the feed rate. Furthermore, the modelling of the column is essential for designing an effective start-up procedure. The column should start up at high temperatures and almost full of

water before introducing the propylene oxide, so that the conditions favour the reaction in all the trays of the column.

More broadly, modelling is an essential tool for understanding, designing, and optimizing complex chemical processes, particularly those exhibiting strong non-linear interactions between reaction, mass transfer, and heat effects. Through rigorous first-principles or hybrid modelling, it is possible to capture the coupled dynamics of phase equilibrium, reaction kinetics, and energy balances that govern process behaviour. This allows engineers to move beyond empirical tuning towards predictive process insight—identifying operational boundaries, estimating sensitivities, and anticipating transitions between different operating modes. Advanced modelling not only enhances process safety and performance but also enables digital twins, model-based optimization, and robust control strategies that reduce costs and environmental impact.

In the case of the reactive distillation column described, custom modelling is crucial to detect and understand the existence of multiple steady states—phenomena that cannot be identified through standard steady-state simulations or plant observations alone. By combining detailed thermodynamic descriptions, reaction kinetics, and tray-by-tray mass and energy balances, AmbarPro's modelling approach can map the full steady-state landscape and identify stability regions. This capability enables:

- The design of more robust and resilient systems
- Safer start-up and shutdown procedures
- Implementation of control strategies that prevent undesired state transitions

Ultimately, custom modelling transforms process data into actionable knowledge, allowing plants to operate closer to their optimal, most productive regimes and providing a clear competitive advantage.

The modelling and numerical techniques demonstrated in this study are representative of the capabilities that AmbarPro applies to industrial projects involving highly nonlinear process units, where standard simulation approaches fail to provide sufficient insight.

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