INTERACTIVE CONTROL ENGINEERING
Principles and Applications

Volume 12 Control in Petrochemicals and Polymers

CHAPTER 6

An Ethylene Oxide Reactor Simulator for Selectivity, Runaway and an Optimum Without a Setpoint

Pages 117–138

Edited by John D. Hedengren

How to cite this chapter. "An Ethylene Oxide Reactor Simulator for Selectivity, Runaway and an Optimum Without a Setpoint," in *Control in Petrochemicals and Polymers*, John D. Hedengren, Ed., vol. 12 of *Interactive Control Engineering: Principles and Applications*. Advanced Process Solutions, LLC, 2026, ch. 6, pp. 117–138.

The page numbers in this file are those of the printed volume.

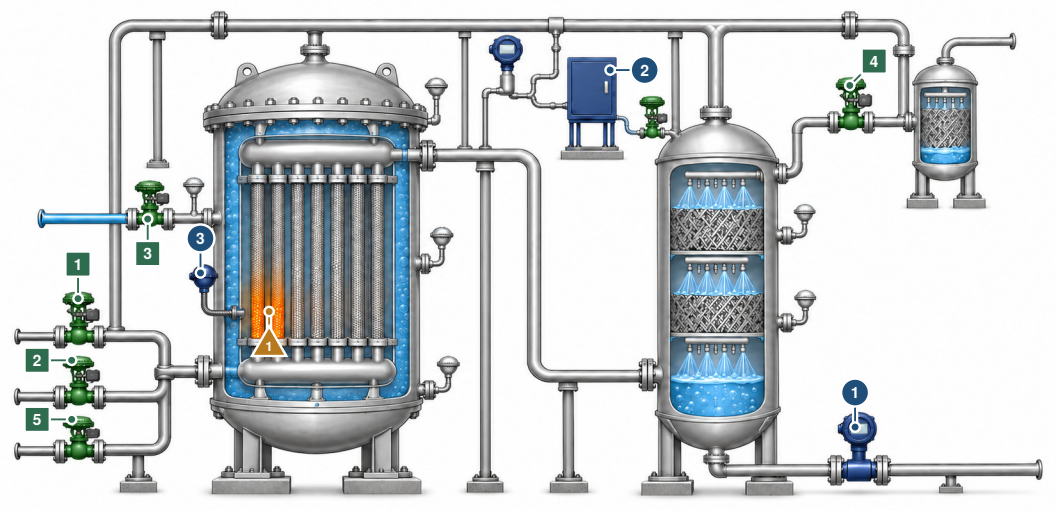
The app for this chapter
https://apmonitor.com/apps/ethylene-oxide/

The volume online: contents, other chapters and citation records
https://apmonitor.com/apps/books/v12-petrochemicals-polymers/#ethylene-oxide

Copyright © 2026 Advanced Process Solutions, LLC. All rights reserved. Produced by Advanced Process Solutions, LLC.

CHAPTER 6

An Ethylene Oxide Reactor Simulator for Selectivity, Runaway and an Optimum Without a Setpoint



The controller moves 1 oxygen feed valve, which sets the production 2 ethylene feed valve 3 coolant valve, for the coolant temperature the oxygen loop sets 4 valve of the carbon dioxide wash 5 chloride dosing valve

The controller reads 1 production meter on the ethylene oxide made 2 cycle gas analyzer for oxygen, ethylene and carbon dioxide 3 hot spot thermocouple, which drives the override

What disturbs it 1 catalyst activity that changes ▲ a wash column that loses circulation

Notice the hot zone inside the tubes, which the controller reaches only through the oxygen feed and the coolant, and which the model gives to every tube alike. Illustration, not to scale.

IN PLAIN TERMS A Reactor Where the Waste Makes the Heat

The main idea. Ethylene oxide is made from ethylene gas and oxygen on silver, in thousands of thin tubes standing in boiling water. The small share of ethylene that burns gives off most of the heat.

The challenge. A tube a few degrees too warm can overheat on its own, while a cooler one leaves spare oxygen nearer to catching fire. A trace of a chlorine compound helps the silver up to a point, and a simple controller cannot tell which side of that point the plant is on.

Why it matters. The plant must make product while it keeps clear of two dangers that pull opposite ways.

THREE WAYS TO READ THIS CHAPTER

Explore	12 min	This page, the History boxes in Section 6.2, the Did you know? boxes in Sections 6.1 and 6.5, the Try it boxes in Section 6.5, and Key points in Section 6.9. No equations.
Study	40 min	The whole chapter in order, stopping at the three pause points, then Exercises 1 to 12.
Practice	15 min	This page, Section 6.5 with Figure 6.2, Section 6.6, and Section 6.7 with its Open challenge box.

The control question On an ethylene oxide reactor the eighth of the ethylene that burns makes two thirds of the heat, the cool steady state of the tube ends a few degrees above the design coolant, and the chloride that sets the selectivity has a maximum. Which handle protects which limit, what keeps the reactor off its cliff, and why can no fixed-sign loop hold the chloride at its optimum?

Learning objectives

- Compute the heat share of the unwanted reaction and explain why the reactor runs hotter as it makes less product.
- Locate the end of the cool steady state on the open tube, and explain how the recycle loop holds the reactor off it and why it still overshoots.
- Justify pairing production with the oxygen feed and an override that cuts the rate rather than the coolant.
- Explain why one chloride PID settles below the selectivity maximum and walks to a trip above it, and compute the resolution of a step search.
- Evaluate an economic predictive controller against a fixed chloride policy on production, margin and oxygen tracking.

Prerequisites Sections 1.4.3 (selectivity and runaway), 1.4.8 (one-way guards and back-off), 1.6.2 (velocity-form PID), 1.6.3 (predictive control option) and 1.6.4 (scenarios and Reset).

The app https://apmonitor.com/apps/ethylene-oxide/

See also Volume 7, Chapter 2 for an ignition boundary a few kelvin from the operating point, and Volume 7, Chapter 4 for a setpoint at the peak of a plant characteristic. Volume 4, Chapter 2 and Volume 4, Chapter 6 for protective overrides on a hard limit. Volume 9, Chapter 8 for a supervisory layer that chooses setpoints under a moving optimum, and Volume 9, Chapter 4 for offset-free predictive control with a disturbance estimate.

6.1 Introduction

A selectivity of 87.2 % sounds like a process in which the unwanted reaction is a detail. On an ethylene oxide reactor it owns the energy balance. Epoxidation releases 105 kJ/mol of ethylene and complete combustion releases 1327, so the 12.8 % of the ethylene that burns produces 65 % of the 40 MW coming off the tube bundle. Everything difficult about the unit follows from that ratio. The reactor is nine thousand narrow tubes standing in boiling water because the heat has to leave within a centimeter of where it is made. The combustion carries the larger activation temperature, 11 800 K against 8200, so it accelerates faster with every degree, which means the reactor gets hotter because it is making less of what is wanted. Section 1.4.3 derives this split for two parallel reactions in general, on the small oxidation tube of the running example.

+ DID YOU KNOW? Carbon Dioxide for Every Tonne of Oxide

Carbon dioxide is the main side product of ethylene oxide, 0.2 to 0.3 tonnes for every tonne of oxide. Industrial reactors convert only 7 to 15 percent of their ethylene on each pass, because the selectivity falls as the conversion rises [1]. In the reactor of this chapter 12.8 % of the ethylene burns.

The misconception the simulator corrects is that a minority reaction is a minor term. A second one follows. Measured on the model at the design gas composition, 4.2 °C above the design coolant temperature the tube has no cool steady state at all: the peak goes from 267.0 °C at 244.8 °C of coolant to 290.1 °C at 248.8, and from 248.97 °C the nearest solution is on the far side of seven hundred. That is parametric sensitivity, the classical property of a fixed bed in which a small parameter change produces a disproportionate change in the peak temperature [2, 3], and the safe region ends at a point rather than tapering. Volume 7, Chapter 2 measures the same contrast of exponential generation against linear cooling on a jacketed stirred tank, which can ignite after a jacket change of a few kelvin.

A third result is the one worth the most. The recycle loop around the reactor is a stabilizer: burning more oxygen leaves less oxygen to burn. Measured with the coolant fixed in manual and the override off, a thirty-five percent catalyst activity step settles the tube back at 267.6 °C on 5.68 mol% oxygen instead of 7.20, on a catalyst that would ignite a once-through tube. The recycle is worth more to this reactor than any controller on it, and a single-tube analysis would badly overstate how fragile the unit is. It also arrives late. The tube answers in about a minute and the loop takes eight minutes to turn over once, so the peak reaches 286.6 °C on the way, nineteen degrees past where it ends up and eight past the alarm.

This chapter works with an interactive ethylene oxide reactor whose kinetics, chloride response and flammability correlation are hidden, so that the energy split must be read from the model, the sensitivity boundary set against the recycle loop that keeps the reactor off it, and a chloride optimum approached by a method other than a controller. Its scenarios include one in which an identical PID controller settles from one side of an optimum and another in which it trips the reactor from the other. The epoxidation kinetics, parametric sensitivity and override control are established subjects, and the chapter applies them to one plant.

The chapter is organized as follows. Section 6.2 recalls how the process came to be a history of selectivity and the three features that set its control problem. Section 6.3 states the twelve-cell multitubular reactor inside its recycle loop, with its chloride dynamics and its moving flammability limit, in the detail needed to rebuild it. Section 6.4 describes the regulatory loops, why production is paired with the oxygen feed, the override that acts on the rate, the three ways to set the chloride and an optional economic model predictive controller. Section 6.5 reports the measured results, from the energy split and the cliff through the recycle, the chloride optimum, the search and the two conflicting margins to the graded challenge and the comparison with predictive control. Section 6.6 names the hardware and the practice behind the model. Sections 6.7, 6.8 and 6.9 state the limitations, the three lessons that carry beyond epoxidation and a summary, and the exercises follow in Section 6.10.

6.2 Background

Ethylene oxide is made at a scale of tens of millions of tonnes a year and is the starting point for ethylene glycol, polyester and most nonionic surfactants. Direct oxidation over silver replaced the chlorohydrin route, as the History box below tells, and the entire subsequent history of the process is a history of selectivity. Early silver catalysts reached the mid seventies of a percent. Modern high selectivity catalysts reach the high eighties, and the improvement came from promoters: cesium, rhenium and the chloride moderator that is the subject of four of the chapter's scenarios [4].

> ⧖ HISTORY **From Chlorine to Oxygen, 1937 and 1958**
>
> The route that direct oxidation replaced was a costly two-stage one. Ethylene reacted in the liquid phase with hypochlorous acid to an ethylene chlorohydrin, which hydrated lime then turned into the oxide, with a selectivity of about 80 percent and with ethylene dichloride and calcium chloride as unwanted by-products. Industrial production by direct oxidation started in 1937 with a process that fed ethylene and air, and in 1958 processes fed with oxygen instead of air were introduced. Air plants had to send part of their recycle gas to a second purge reactor, and they emitted more and yielded less. The price of chlorine and the effluent load retired the old route, and in 2013 the oxygen route was the only one in use in the European Union [5].

Three features set the control problem.

The first is the heat. The reactor is multitubular with boiling coolant on the shell, and heterogeneous models of industrial reactors of this type resolve the axial profile because the peak is what matters [6]. Parametric sensitivity is the property that governs how close such a reactor can be run to its limit, and the criteria for it were developed for fixed beds generally [2, 3] and are surveyed across chemistries in the safety literature [7].

Table 6.1 Classification of Variables at the Design Operating Point

Symbol	Role	Nominal	Range
EO rate	CV, continuous	8.00 kmol/min	2–12 SP
y_O	CV, analyzer	7.20 mol%	4–9 SP
y_E	CV, analyzer	24.00 mol%	15–32 SP
y_C	CV, analyzer	5.00 mol%	2–12 SP
T_{hot}	constraint	267.1 °C	alarm 278, trip 296
y_O^{lim}	constraint	8.60 mol%	moves
F_O	MV	7.606 kmol/min	0–14
T_c	MV	244.8 °C	200–280 °C
F_E	MV	9.461 kmol/min	0–18
w	MV	67.3 %	0–100 %
Cl	MV, optimizing	2.50 ppm	0–8 ppm
activity	DV, unmeasured	1×	0.55–1.5×
T_i, y_E, y_O, y_C, Cl	states	—	—

HISTORY Heat Made Against Heat Removed, 1928 to 1970

The picture behind this chapter's cliff is older than the process. In 1928 Semenov considered an exothermic reaction and drew the heat it releases, which rises exponentially with temperature, against the heat removed by heat transfer, which rises linearly. His diagram has a stable operating point and a critical one, and a coolant warmer than the critical value lets the reaction ignite itself. That work laid the groundwork for a run of runaway criteria. In 1970 van Welsenaere and Froment set critical conditions for fixed beds from the locus of temperature maxima, and Morbidelli and Varma drew the boundary where the reactor becomes sensitive to small changes in its inputs [7].

The second is the flammable envelope. The cycle gas is oxygen and hydrocarbon in one vessel at fifteen bar, kept out of the flammable region by ballast, and the limiting oxygen concentration is a function of the gas rather than a constant. Flammability limits move with temperature, pressure and diluent, and their determination at elevated conditions is its own experimental problem [8], with estimation methods used where measurement is impractical [9]. The practical consequence for control is that an oxygen controller holding a fixed setpoint is holding a moving margin. Volume 4, Chapter 6 guards a solvent vapor limit in a dryer with an override of the same one-directional kind.

The third is the chloride. A few parts per million of an organic chloride on the silver block the sites that burn ethylene, and the benefit saturates. The same chloride blocks the sites that do anything at all, and that penalty does not saturate. The result is a selectivity curve with a maximum, and the industrial practice of finding and holding that maximum is one of the oldest real-time optimization problems in the chemical industry. It is solved by periodic perturbation rather than by feedback, for the reason Section 6.5 measures.

Above all of it, a modern plant carries a multivariable controller that arbitrates between production rate, selectivity and the two constraints [10]. The application implements that regulatory layer and an optional economic MPC.

6.3 Process Model

Reactor R-501 is a bundle of 9200 tubes carrying 3.10 kg of silver catalyst each, in boiling coolant at 244.8 °C. Cycle gas at 205 °C enters at 320 kmol/min carrying 24.00 mol% ethylene, 7.20 mol% oxygen and 5.00 mol% carbon dioxide in a methane ballast, and makes 8.00 kmol/min of ethylene oxide at 87.21 % selectivity. Figure 6.1 shows the arrangement.

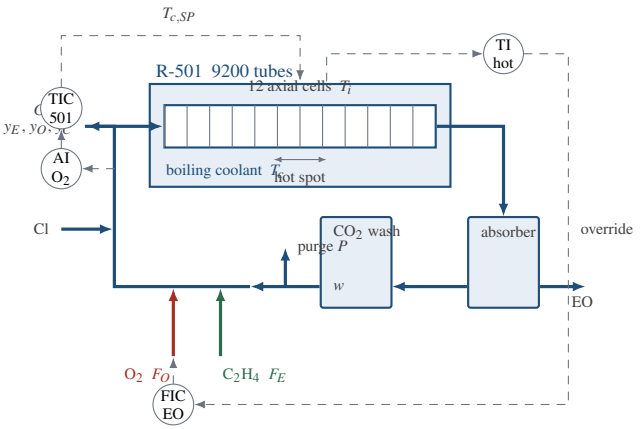


Figure 6.1 Ethylene oxide reactor R-501 inside its recycle loop. Cycle gas G of composition y_E, y_O and y_C enters twelve axial cells at temperatures T_i, cooled by boiling coolant at T_c. Product is washed out in the absorber, a slipstream w removes carbon dioxide, a purge P leaves, and fresh oxygen F_O, ethylene F_E and chloride Cl are added before the gas returns. TIC-501 holds the cycle gas oxygen by moving the coolant setpoint $T_{c,SP}$, FIC-EO holds production on the oxygen feed, and the hot spot thermocouple drives a one-directional override on the production setpoint.

6.3.1 Two Reactions on the Same Sites

Both reactions are first order in oxygen and half order in ethylene, inhibited by carbon dioxide, Equations (6.1) and (6.2).

$$r_1 = k_1 e^{-E_1/RT}\, y_O \sqrt{y_E}\, \phi\, \phi_{act} \tag{6.1}$$

$$r_2 = k_2 e^{-E_2/RT}\, y_O \sqrt{y_E}\, \phi\, \phi_{act}\, (1 - \beta_{Cl}) \tag{6.2}$$

with $E_2/R = 11\,800\,\mathrm{K}$ and $E_1/R = 8200\,\mathrm{K}$, and $\phi = 1/(1+4.6\,y_C)$ the carbon dioxide inhibition. The single difference between the two activation temperatures is why selectivity falls with temperature: the reaction that destroys the product is the one that accelerates faster. Since the two rates share their composition terms, their ratio depends on temperature alone, as Equation (1.4) states.

The heat released follows Equation (6.3), and the ratio in it governs the whole reactor. Weighted by these heats, the heat generated rises with temperature as one reaction with the effective activation of Equation (1.5).

$$q = r_1\,\Delta H_1 + r_2\,\Delta H_2, \qquad \frac{\Delta H_2}{\Delta H_1} = \frac{1327}{105} = 12.6 \tag{6.3}$$

🕮 **Pause.** Try Exercise 6.1 before reading on.

6.3.2 One Axial Cell and the End of the Cool Branch

Each cell balances generation against two removal terms, Equation (6.4).

$$C\,\frac{\mathrm{d}T_i}{\mathrm{d}t} = q_i - \dot{n} c_p (T_i - T_{i-1}) - UA\,(T_i - T_c) \tag{6.4}$$

Generation is exponential in temperature and both removal terms are linear in it, so the steady-state residual has one, two or three roots, the construction of heat generated against heat removed in Section 1.4.3. The working reactor is on the lowest of them, and the steady-state solver that initializes each case solves for it by scanning upward and taking the first sign change rather than by iterating, because a fixed point iteration converges to whichever root it happens to find. Where no crossing

Table 6.2 Model Parameters

Symbol	Meaning	Value	Class
E_1/R	epoxidation activation	8200 K	adjustable
E_2/R	combustion activation	11 800 K	adjustable
ΔH_1	heat of epoxidation	105 kJ/mol	adjustable
ΔH_2	heat of combustion	1327 kJ/mol	adjustable
UA	coolant transfer per cell	0.0200 kW/K	adjustable
β_{max}	burning blocked at saturation	0.80	adjustable
$\mathrm{Cl}_{1/2}$	chloride for half of it	1.20 ppm	adjustable
k_{Cl}	activity lost per ppm	0.340 per ppm	adjustable
τ_{Cl}	chloride uptake	55 min	adjustable
G	cycle gas circulation	320 kmol/min	adjustable
holdup	gas in the loop	2450 kmol	adjustable
θ	selectivity analyzer cycle	30 min	adjustable
T_{hot} alarm	hot spot alarm	278 °C	visible

exists the tube has no cool steady state, and the solver returns an explicit runaway flag rather than a hot root. A setting chosen before a run starts it at that setting’s steady state, unless the protection would trip on that state at once, in which case the run starts at the case’s own state and the setting acts from $t = 0$. The coolant helper and the shipped checks read that flag, while the running simulation integrates Equation (6.4) for all twelve cells with $C = \dot{m} c_p \tau_{tube}$ and $\tau_{tube} = 1.15\,\mathrm{min}$.

6.3.3 The Chloride Curve

Chloride blocks the burning sites with a benefit that saturates and all sites with a penalty that does not, Equations (6.5) and (6.6).

$$\beta_{Cl} = \frac{\beta_{max}\,\mathrm{Cl}}{\mathrm{Cl}_{1/2} + \mathrm{Cl}} \tag{6.5}$$

$$\phi_{act} = e^{-k_{Cl}\,\mathrm{Cl}} \tag{6.6}$$

A saturating good against a compounding bad is a curve with a maximum, and a maximum is a place where the process gain is zero and changes sign.

6.3.4 A Limit of Flammability That Moves

The limiting oxygen concentration is not a constant. Ethylene is the fuel and lowers it, and carbon dioxide is a heavy inert and raises it, Equation (6.7).

$$y_O^{lim} = y_0 - a\,(100 y_E - 24) + b\,(100 y_C - 5) \tag{6.7}$$

The correlation is a straight line fitted near the design composition and is clamped outside the range where it was fitted, because an extrapolated line is a fiction. The consequence for control is that the carbon dioxide the wash column removes for activity reasons is the same carbon dioxide that keeps the loop out of the envelope.

6.3.5 Assumptions

One tube stands for 9200 and the bundle is assumed identical. Real bundles have a distribution of flow and packing, and a runaway starts in the tube at the end of that distribution rather than in the average one.

Twelve lumped axial cells replace a distributed profile, so the hot spot is located to about one twelfth of a tube and the model understates the true peak.

Two lumped reactions represent a network that also makes acetaldehyde and can burn the oxide once formed.

The chloride effect is a fitted shape rather than a site balance, with one first-order lag. Real chloride behavior depends on the hydrocarbon carrying it and has a memory measured in days [4].

The gas loop is one well stirred tank with no transport delay. A real loop is an absorber, a compressor and a wash column in series.

The flammability limit is linear in two compositions and clamped. Real envelopes are measured surfaces applied with a margin nobody negotiates [8, 9].

6.4 Controller Design

6.4.1 Velocity Form PID

Every loop uses the shared velocity-form PID of Section 1.6.2, Equations (1.14) to (1.17), with back-calculation anti-windup on the integral alone and the tracking time $T_t = \tau_I$. Every loop here runs with $\tau_D = 0$, so only the proportional and integral increments appear. The action is $a = -1$ for the oxygen loop, because a hotter coolant leaves less oxygen in the cycle gas, and for the carbon dioxide loop, because more wash leaves less carbon dioxide. It is $a = +1$ for the production, ethylene and chloride loops. A loop in manual tracks the output actually held, which makes the return to automatic bumpless, and during a trip, which forces the feeds to zero and the wash to full, every loop tracks the forced values in the same way.

One limit acts after the PID output and is unknown to it. A carbonate wash that has lost circulation caps the applied slipstream below the 100 % the carbon dioxide loop believes it has. With half the circulation lost (scenario 11) that loop commands 100 % from 68 min onward while 50 % reaches the column, and its integral settles at 100 % with a demanded output, the output before limiting v_k of Equation (1.16), of 157 %, back-calculated against its own limit rather than against what the column delivers. The controller scan is 0.05 min and integration is fixed-step fourth-order Runge-Kutta at 0.01 min (Section 1.6.1).

6.4.2 Why Production Is on the Oxygen Valve

At steady state in a closed recycle loop every oxygen molecule fed is either reacted or purged, Equation (6.8), so the oxygen feed sets the production rate and the coolant temperature cannot.

$$F_O = \dot{n}_{O_2,reacted} + P\,y_O \tag{6.8}$$

Measured in scenario 2 with the oxygen feed fixed and the ethylene and carbon dioxide loops holding, two degrees of extra coolant, stepped 10 min into the run, moves production from 8.00 kmol/min to 7.91 kmol/min within two hours, and the cycle gas oxygen settles at 6.80 mol% instead of 7.20. Production first rises to 8.43 kmol/min within eight minutes and then falls back as the loop composition thins, so the coolant has gain on the rate only for about one loop turnover. At steady state with every feed fixed the same two degrees give 7.91 and 6.22 mol%. What the coolant sets is where the loop composition comes to rest, which is to say how much unreacted oxygen is standing in a fifteen bar loop that must never be flammable, and that is a more important thing for it to decide than the rate.

6.4.3 The Override Acts on the Rate

Cooling the reactor would bring the hot spot down and would leave more unreacted oxygen in the cycle gas, walking the loop toward the envelope. The two constraints want opposite things from the coolant valve. At steady state with every feed fixed, cooling from 244.8 °C to 241.0 °C takes the hot spot from 267.1 °C to 262.5 °C and takes the oxygen margin from 1.40 mol% to −0.50 mol%, while heating to 248.8 °C gives 272.0 and 1.82. The only handle that moves both margins the right way is the oxygen feed, and it is the one that costs money. The override is therefore one-directional on the production setpoint, Equation (6.9), one of the fast one-way guards of Section 1.4.8.

$$\mathrm{EO}_{SP} \leftarrow \mathrm{EO}_{SP} - K_o\,[T_{hot} - (T_{alarm} - m)]^{+} \tag{6.9}$$

The default gain is $K_o = 0.35\,\mathrm{kmol/min}$ per degree and the margin $m = 8\,^{\circ}\mathrm{C}$. The trimmed value is the setpoint of the production loop, so the override reaches the oxygen valve through that loop rather than through any integral state, and T_{hot} is the model's hottest cell with no thermocouple lag.

Pause. Try Exercise 6.3 before reading on.

6.4.4 Three Ways to Set the Chloride

With the Loops supervisor selected, the application offers manual, a PID on the selectivity analyzer, and a step and search optimizer. Only two of them can work, and Section 6.5 measures which.

6.4.5 Economic Model Predictive Control

Section 1.6.3 describes the predictive option of the framework. This one differs in its objective, which prices production and selectivity instead of weighting the distance from setpoints. The optional MPC coordinates $u = [F_O, T_{c,SP}, \mathrm{Cl}_{feed}]$ while the ethylene and carbon dioxide PI loops remain regulatory. Manual handles remain fixed. A 19-state nominal model contains the 12 cell temperatures, coolant, three recycle fractions, catalyst chloride, and two regulatory commands. Central differences of the declared balances at the design point, rather than current plant parameters or hidden activity, supply the affine matrices A_d, B_d, E_d, c_d, C_d in Equation (6.10).

$$x_{k+1} = A_d x_k + B_d v_k + E_d \hat{d}_k + c_d, \qquad \hat{y}_k = C_d x_k + y_0 \tag{6.10}$$

Here x and v are state and command deviations, $\hat{d}$ contains estimated constant disturbances, and y comprises EO rate, selectivity in percentage points, cell-8 temperature, oxygen, and oxygen minus its flammability limit. The first four disturbances enter through E_d, while the fifth shifts the hot output in y_0. Known regulatory setpoints and purge enter the affine term. Symmetric nonlinear steps of ± 0.1 kmol/min oxygen feed, ± 0.5 °C coolant and ± 0.25 ppm chloride give at most 0.547% dominant-output response error at 20, 60 and 180 min. This is local validation, not an ignition model.

The first solve occurs at $t = 0$. Thereafter $T_s = 2$ min spans 40 unchanged controller scans. The 180 min horizon has $N = 90$ steps with move blocks $[1, 1, 2, 4, 8, 16, 58]$, or 21 command decisions. A constrained quadratic program [11] minimizes

$$\begin{aligned} J = \sum_{k=1}^{90} T_s[-a_E \hat{E}_k - a_S \hat{S}_k + a_S \kappa (\mathrm{Cl}_{feed,k} - \mathrm{Cl}_*)^2] \\ + \sum_{b=1}^{7} \sum_{i=1}^{3} 0.1(\Delta u_{i,b}/s_i)^2 + \sum_j (\alpha_j \varepsilon_j + \beta_j \varepsilon_j^2). \end{aligned} \tag{6.11}$$

The local derivatives of $M = E - 0.62E/(S/100)$ are $a_E = 0.289083$ and $a_S = 0.065215$, where E is EO in kmol/min and S is percent selectivity. The declared chloride curve gives $\mathrm{Cl}_* = 2.492825$ ppm and $\kappa = 0.348829$ percentage points/ppm^2. The block-boundary move Δu uses scales $s = [0.1\ \mathrm{kmol/min}, 1\,^{\circ}\mathrm{C}, 0.1\ \mathrm{ppm}]$. A 10^{-7} Hessian ridge regularizes the program. There is no terminal cost or disturbance preview.

Command boxes are hard: $0 \le F_O \le 14$ kmol/min, $200 \le T_{c,SP} \le 280$ °C and $0 \le \mathrm{Cl}_{feed} \le 8$ ppm. Production and oxygen requests are soft upper bounds, with $(\alpha, \beta) = (10^3, 10^3)$. The hot bound is 1 °C below the override start, 269 °C in the new case. The oxygen-envelope bound backs off 0.2 mol% from the existing trip guard. Both use $(10^4, 10^3)$. Each bound L_j initially expands to $L_j + [\hat{y}_{j,0} - L_j]^+ \exp(-kT_s/10)$. One nonnegative ε_j per bounded output is shared across the entire horizon. Excess above this funnel can therefore persist up to that same slack without a separate later penalty. These priced bounds do not guarantee nonlinear plant constraint satisfaction. The override and trip retain authority.

A steady-state Kalman gain corrects 17 physical states plus five constant states for activity, the three gas balances and hot-spot offset [12]. Its five readings are EO, oxygen, ethylene, carbon

Table 6.3 Hot Spot Against Coolant Temperature at Design Composition

Coolant (°C)	Hot spot (°C)
244.8	267.0
246.0	271.0
248.0	281.0
248.8	290.1
248.9	293.6
249.0	no cool solution (741)

dioxide and the hottest cell. Selectivity and hidden activity are not measurements. The diagonal process covariance is 10^{-4} for each temperature, 10^{-10} for each gas fraction and 10^{-6} for chloride. Disturbance variances are $[10^{-5}, 10^{-10}, 10^{-10}, 10^{-10}, 10^{-2}]$. Measurement variances are the squares of $[0.02, 0.03, 0.05, 0.03, 0.1]$ in the native measurement units, in the stated order. Known applied commands drive prediction, including the commanded wash before its unmeasured failure cap. The instrument filters remain in the simulation but are omitted from the controller model. Disturbance estimation corrects prediction offsets, but economic ceilings do not enforce zero setpoint error. The losing PIDs track applied commands. A rejected, nonfinite or out-of-range plan returns authority to those loops, marks fallback, and resumes MPC after a valid solve. Chloride search waits a full dwell on handover.

6.5 Results

Thirteen scenarios run from the energy split to a graded challenge, in the order the app lists them: 1, “Which reaction makes the heat” (the energy split), 2, “Five loops and what each one owns” (pairing in a recycle), 3, “The hot spot is not the outlet” (moving constraints), 4, “Where the cool solution stops existing” (parametric sensitivity), 5, “The recycle is the real stabilizer” (slow negative feedback), 6, “Chloride, in both directions” (a flat maximum), 7, “A PID above the optimum” (positive feedback), 8, “The same controller below it” (conditional correctness), 9, “Step, wait, compare, reverse” (search resolution), 10, “Two margins, opposite directions” (constraint conflict), 11, “The wash column is a safety device” (inert double duty), 12, “The reaction you do not want, priced” (economic coordination), and the challenge, “A shift on a fresh charge”. Scenarios 5 and 7 are demonstrations, and the other ten numbered cases are experiments. Scenarios 7 and 8 differ only in a starting condition and are meant to be run back to back. Each case is credited separately when the learner performs the listed actions and the simulation reaches the listed state (Section 1.6.4). The challenge is judged on the case as given, so changing a model parameter or a disturbance voids the attempt, and the credit accumulates toward certificates of progress and of completion.

> ✦ **DID YOU KNOW? Cooling the Reactor Can Spend the Safety Margin**
>
> From the simulator: with every feed fixed, cooling from 244.8 to 241.0 °C lowers the hot spot from 267.1 to 262.5 °C, and it takes the oxygen margin from 1.40 to −0.50 mol%, past the limit of flammability (Table 6.6). The move that looks safe for the silver is not safe for the gas.

6.5.1 The Energy Split and the Cliff

At the design point the combustion produces 65.0 % of the 40 MW duty at 87.21 % selectivity. Table 6.3 reports the coolant temperature swept on the open tube at the design gas composition.

The cool solution ends at 248.97 °C, so 4.2 °C is the entire distance between the design point and a tube that cannot stand up. The steps accelerate because the exponential was always going to outrun the lines and the only question was where.

Scenario 4 runs the same coolant steps, to 249.4 °C, on the full loop with every station in manual, and the cliff does not appear. The hot spot reads 268.5, 270.8 and 272.4 °C at the ends of the three

Table 6.4 Chloride Against Selectivity and Hot Spot, All Loops Holding

Chloride (ppm)	Selectivity (%)	Hot spot (°C)
1.50	86.77	254.9
2.10	87.15	262.1
2.40	87.21	265.8
2.70	87.19	269.6
3.30	87.01	277.5

Table 6.5 One Chloride PID, Two Starting Points

Start (ppm)	Reaches (ppm)	Outcome
1.50	1.97	still rising at 10 h, 2.09 at 50 h
3.30	4.76	trips on hot spot at 381.8 min

steps (at 60, 110 and 240 min) and never exceeds 273.8 °C, because a hotter tube consumes its own oxygen and the cycle gas falls from 7.20 mol% to 6.33 mol%. The cliff belongs to the tube at fixed composition. What keeps the reactor off it is the subject of the next subsection.

6.5.2 The Recycle Stabilizes and Arrives Late

With the coolant fixed in manual, the override off and the catalyst made thirty-five percent more active at 20 min (scenario 5), the cycle gas oxygen falls from 7.20 mol% to 5.68 mol% by 4 h and the tube settles at 267.6 °C, almost exactly where it started. The production loop stays closed and ends with the oxygen feed at 7.59 kmol/min against 7.61, so the stabilizing action is the loop composition rather than the feed. On the way the peak reaches 286.6 °C at 25.9 min, nineteen degrees past where it ends up and eight past the alarm, and it stays above the alarm for 7 min, because the tube answers in about a minute and the loop takes eight minutes ($2450\,\text{kmol}/320\,\text{kmol/min} = 7.7\,\text{min}$) to turn over once.

> **TRY IT IN THE APP** **5 · The Recycle Is the Real Stabilizer**
>
> Load the scenario, which starts with the oxygen loop in Manual and the override Off, and press Run for four hours. Watch the Hot spot and Cycle gas oxygen plots. The catalyst turns more active at 20 min, the hot spot peaks at 286.6 °C at 25.9 min, and it settles at 267.6 °C as the oxygen falls from 7.20 to 5.68 mol%. The coolant stays fixed throughout.

Both halves of that result matter. A steady-state analysis of this loop says the reactor cannot run away. A dynamic one says the silver has been where silver should not be.

6.5.3 The Chloride Optimum and the Controller That Cannot Hold It

Table 6.4 reports the chloride swept with all four composition and rate loops holding their setpoints and the override off, each value stepped in the feed 10 min into a run from the design point and read 20 h after the step. Scenario 6 reproduces the two ends, 86.77 and 87.01 % with the hot spot at 255.0 and 277.5 °C, at the end of each step (500 and 960 min).

The maximum is near 2.5 ppm (2.49 at the design composition and rate) and it is flat: a part per million either side costs less than half a point of selectivity, 0.45 below and 0.29 above. The hot spot over the same range is not flat at all, moving 22.6 °C. The variable that is nearly invisible in the economics is enormous in the temperature, and it is the temperature that ends the campaign. Figure 6.2 draws the table on one chloride axis.

Now put a PID on it. Table 6.5 reports the same controller, the same setpoint of 87.15 % and the same reactor, started on either side of the maximum.

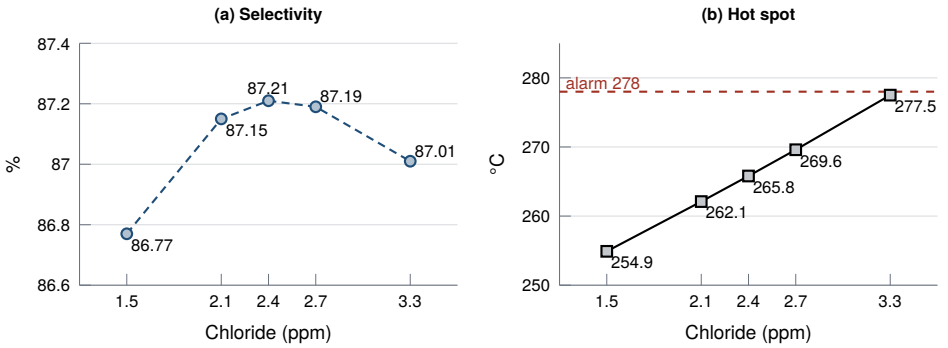


Figure 6.2 The chloride sweep of Table 6.4, with all four composition and rate loops holding. Circles on a dashed line are the selectivity, squares on a solid line the hot spot, and the dashed red line in (b) is the hot spot alarm. Notice the scales: across the whole sweep the selectivity moves less than half a point, while the hot spot climbs 22.6 °C, to 277.5 against an alarm at 278 °C.

Above the maximum the controller pushes chloride up because up is what raises selectivity everywhere it has ever been, and here up lowers it. The error grows, so the controller pushes harder, so the error grows. The loop does not oscillate, it walks, and it walks the coolant up with it until the unit trips. In scenario 7 the hot spot starts at 277.4 °C, passes its alarm at 23.2 min and reaches the 296 °C trip at 381.8 min, with 4.76 ppm on the silver against a command of 5.28 and a coolant request of 272.3 °C. Below the maximum the same controller is stabilizing: in scenario 8 chloride reaches 1.97 ppm at ten hours and 2.09 after fifty hours. Each case starts from its converged feed operating point; the controller and tuning are the same, while the initial compositions follow those different chloride/coolant stations.

> **TRY IT IN THE APP** **7 · A PID Above the Optimum**
>
> Load the scenario, which starts with the chloride on its PID and the override Off, run ten hours and watch the Selectivity and Hot spot trends. The chloride climbs from 3.30 to 4.76 ppm and the unit trips at 381.8 min. Then load scenario 8, “The same controller below it”, and run ten hours more: the same loop brings the chloride to 1.97 ppm and nothing trips.

That is the uncomfortable part. The two runs differ in their starting operating conditions, and nothing in the loop, the tuning, the trend or the alarm list distinguishes the case that works from the case that trips the reactor. A feedback controller assumes the sign of the process gain, and at an optimum the gain is zero and the sign is undefined.

Pause. Try Exercise 6.2 before reading on.

6.5.4 What a Search Can and Cannot Resolve

The step and search optimizer climbs, overshoots, reverses and then hunts across the top forever. Measured over fifty hours from 1.50 ppm it makes twenty-four moves of 0.3 ppm on a two-hour dwell, and after the first ten hours its chloride lives between 1.84 and 2.96 ppm around a true optimum near 2.5, reversing five times. The hunting is not a defect to be tuned out. A search that settles has stopped measuring the gradient.

The width of the hunt follows from arithmetic rather than from tuning. A step of size h at a distance d from a smooth peak changes the objective by roughly $|S''|dh$, so a step can be told from the smallest difference the search trusts, σ, only where $d > \sigma/(|S''|h)$. Here the curvature is about 0.7 % of selectivity per part per million squared, the step is 0.3 ppm and the search ignores differences under 0.04 %, so no step within about 0.2 ppm of the top can be resolved. The chloride uptake (55 min) and

Table 6.6 The Two Constraints Move Opposite Ways With the Coolant

	All feeds fixed		Scenario 10	
Coolant (°C)	Hot spot (°C)	O_2 margin (mol%)	Hot spot (°C)	O_2 margin (mol%)
241.0	262.5	−0.50	262.8	0.52
244.8	267.1	1.40	267.1	1.40
248.8	272.0	1.82	271.6	2.18

the half-hourly analyzer let only part of each step register before the two-hour dwell ends, which is why the turns come at 1.8 and 3.0 ppm, about two steps either side of the top. With 0.5 % of analyzer noise $\sigma/(|S''|h)$ exceeds two parts per million, and the second half of scenario 9 shows it: ten reversals in two days instead of five and, after the first ten hours, a band of 1.54 to 2.66 ppm on the shipped noise sequence, while one of four other sequences wanders from 0.02 to 4.67 ppm. The consolation is in the same arithmetic. The optimum is flat because the curvature is small, so half a part per million off costs less than a tenth of a point, and the quiet hunt averages 87.16 % against 87.21 at the peak.

6.5.5 Two Margins in Opposite Directions

The fixed-feed solver now closes all three material balances to below 10^{-9} kmol/min. The cold equilibrium is outside the oxygen envelope; it is not a safe operating point. Runs with no safe fixed-feed equilibrium use a safe case composition line-up, or the declared design point if no such line-up exists, with the chosen stations acting from $t = 0$. Table 6.6 reports the coolant swept twice, as a steady state with every feed fixed and as scenario 10 runs it, with the production and oxygen loops open and the ethylene and carbon dioxide loops holding their compositions, read at the end of each step.

With the ethylene and carbon dioxide held at their setpoints the limit of flammability stays near 8.6 mol%, so the scenario loses less margin on the cold side, but the two margins still move in opposite directions. The hot step is also not gentle in the run. The hot spot reaches 286.4 °C 11 min after the coolant goes to 248.8 °C and stays above its alarm for 10 min before settling. With the two loops then closed and the override on, the rate is trimmed for only 6 min while the oxygen loop takes the coolant back.

No direction of coolant movement improves both margins at once. Cutting the oxygen feed moves both the right way and costs production, which is why the override acts there. When two constraints conflict on a handle, the move that relieves both is almost always the one that gives up the objective.

6.5.6 The Graded Challenge

The challenge runs fifteen hours on a fresh catalyst charge that becomes more active twice, with a carbonate wash that loses part of its circulation, with cautious tuning and three structural decisions switched off. It is met when the cycle gas oxygen is held within 0.12 mol% of setpoint through the last third, from 594 min to the end, the hot spot stays below its 278 °C alarm throughout, and the unit does not trip. The shipped settings miss the oxygen band, with a worst late error of 0.314 mol%; the suggested settings pass at 0.105 mol%. Their hot-spot peaks are 272.6 and 274.4 °C, with no trips. On seeds 1–4 the suggestion gives 0.137, 0.083, 0.109 and 0.092 mol%; one of the four fails. Retuning only the oxygen loop ($K_c = 7$, $\tau_I = 18$ min) passes at 0.077 mol%, but leaves only 1.56 mol% of oxygen margin at the end, against 1.75 for the full suggestion. Leaving composition loops in manual with the other suggested settings leaves 1.59. Restoring the chloride to 2.50 ppm raises final selectivity by 0.21 points but also raises the final hot spot by 8.4 °C.

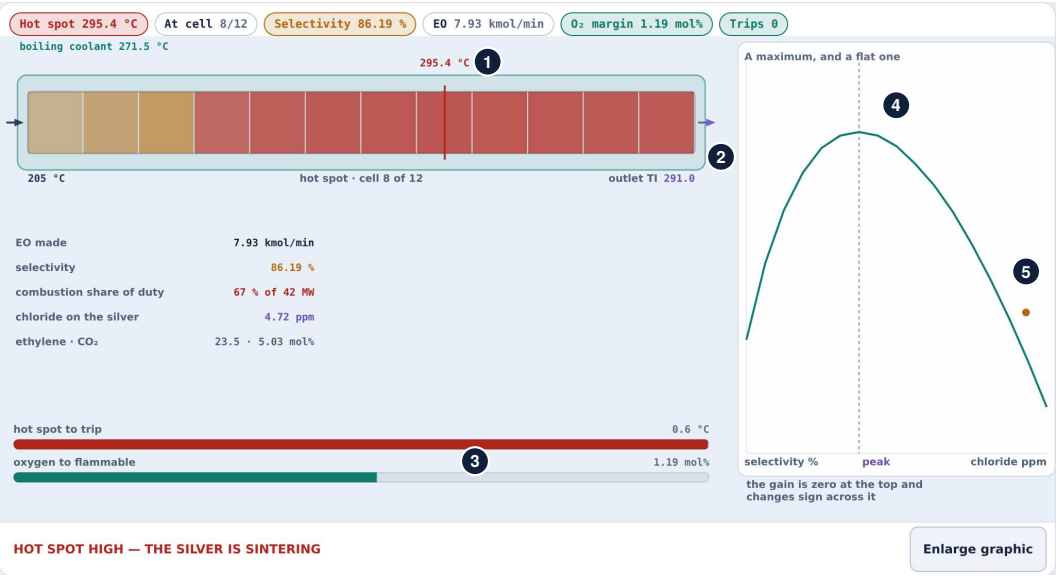


Figure 6.3 The ethylene oxide application running scenario 7, the chloride PID started above the optimum with the override off, at 378 min, about four minutes before the trip. One tube is drawn the long way with its twelve axial cells shaded by temperature and the hot spot marked where it is (1), 295.4 °C in cell 8 of 12 against 291.0 °C at the outlet thermocouple (2). Bars under the tube (3) show the two margins, 0.6 °C from the hot spot to its trip and 1.19 mol% from the cycle gas oxygen to the limit of flammability. The inset draws the model's selectivity against chloride at the design composition and rate, with its peak marked at 2.5 ppm (4), and places the present operating point (5), 4.72 ppm and 86.19 %, far to the right of the peak and 0.2 points above the curve, which is drawn for the design gas.

6.5.7 Measured Economic and Tracking Trade-offs

Case 12 reduces activity from 1.00 to 0.85 at 60 min and raises the rate request from 8.0 to 8.8 kmol/min at 240 min. Table 6.7 uses seed 20260921, identical instruments, noise, events and initial conditions, with no preview or case-specific MPC retuning. The search case runs 2880 min and the other rows run 900 min. EO and oxygen IAE use the shared scorecard definitions. The EO total is the application's own scorecard total, the left-rectangle sum of the rate in kmol/min over the 0.01 min physics steps while the unit is not tripped. The reported $\bar{M}$ is the time average of $E - 0.62C_2$used in product-equivalent kmol/min, not dollars per hour.

MPC yields $\bar{M} = 2.338943$, against 2.093185 with search and 2.340381 with the best tested fixed-chloride policy. Its deficit to that comparator is 0.06145%, a near tie. The hindsight sweep tests 1, 1.25, 1.5, 1.75, 2 and 2.25 ppm, selecting 1.5 ppm after the first 0.01 min step so the initial state is shared. The two lowest settings trip. MPC makes 7706.8 versus 7689.2 kmol and peaks at 269.783 versus 271.529 °C, but oxygen IAE rises from 35.081 to 76.098 mol%·min. All four main policies spend zero minutes above the alarm or oxygen trip guard; this comparison establishes no alarm-avoidance advantage. Oxygen-feed travel is 5.099 versus 7.992 kmol/min, and coolant travel 16.371 versus 30.108 °C.

The wash case with manual chloride remains a loss: MPC EO IAE is 68.884 versus 3.216 kmol; automatic chloride reduces it to 1.060. Both suggested challenge policies pass. Their oxygen IAE is 57.908 for MPC and 54.131 for loops, and mean margins are 2.329 and 2.322. Their worst late errors are 0.053 and 0.105 mol%; shipped MPC misses at 0.198 mol%.

Table 6.7 Measured Control Comparison With Unchanged MPC Settings

Case	Policy	EO IAE kmol	O_2 IAE mol%·min	Peak hot °C	EO total kmol	$\bar{M}$ equivalent	V_{F_O} kmol/min	V_{T_c} °C	Alarm min	Plans/ rejected	Mean ms
12	Search	1171.42	53.95	277.73	6567.5	2.093185	23.31	44.45	0.00	0/0	0.00
12	Fixed 2.5 ppm	711.99	29.05	277.14	7026.9	2.215296	25.31	42.65	0.00	0/0	0.00
12	Hindsight 1.5 ppm	74.44	35.08	271.53	7689.2	2.340381	7.99	30.11	0.00	0/0	0.00
12	MPC	31.48	76.10	269.78	7706.8	2.338943	5.10	16.37	0.00	450/0	1.39
3	Loops, manual Cl	34.75	15.57	274.15	7201.7	2.370899	5.75	15.20	0.00	0/0	0.00
3	Loops, search	52.09	68.29	274.15	7200.9	2.367571	7.17	36.75	0.00	0/0	0.00
3	MPC, manual Cl	21.97	15.06	273.44	7199.2	2.370326	2.46	10.92	0.00	450/0	1.34
3	MPC, auto Cl	20.79	15.05	273.45	7201.9	2.370540	2.53	10.61	0.00	450/0	1.19
11	Loops, manual Cl	3.22	5.65	269.93	7197.0	2.291114	0.17	2.23	0.00	0/0	0.00
11	MPC, manual Cl	68.88	1.16	269.00	7131.2	2.275079	0.39	1.82	0.00	450/0	1.38
11	MPC, auto Cl	1.06	1.48	269.00	7199.2	2.291223	0.26	1.36	0.00	450/0	1.38
9	Search	101.86	220.53	273.28	23039.4	2.308247	9.38	95.86	0.00	0/0	0.00
9	MPC	6.52	55.05	267.30	23045.1	2.310983	1.30	14.43	0.00	1440/0	1.36
2	Search	1165.78	46.10	278.09	6706.5	2.165959	18.04	31.62	9.96	0/0	0.00
2	MPC	13.40	0.94	269.22	7860.1	2.476808	1.37	6.33	0.00	450/0	1.40
13	Loops, shipped	85.91	412.24	272.56	7211.4	2.310520	1.30	31.16	0.00	0/0	0.00
13	Loops, suggested	103.54	54.13	274.41	7188.3	2.322046	15.42	112.31	0.00	0/0	0.00
13	MPC, shipped	48.12	92.99	272.76	7243.0	2.331915	11.20	27.45	0.00	450/0	1.21
13	MPC, suggested	44.06	57.91	271.00	7218.5	2.329163	14.14	28.48	0.00	450/0	1.24

Case 12 is aging plus a rate request, case 3 fresh catalyst, case 11 wash loss, case 9 chloride search, case 2 a rate request at 60 min, and case 13 the unchanged challenge. V is total command variation from the scorecard. $\bar{M}$ is normalized product-equivalent kmol/min. The hindsight row selects the best of six fixed chloride settings after the first 0.01 min step, preserving the initial state but using foreknowledge. Zero values in the final column indicate no optimization. Times depend on the host. Every row has zero oxygen trip-guard duration and zero oxygen-feed and coolant hard-bound saturation.

Removing only the chloride-curvature cost still causes a late trip. A production-only objective makes 7717.7 kmol but lowers mean margin to 2.277, against 2.339 for MPC. Halving the physics step changes MPC product by -0.000493 kmol and mean margin by $-6.33e-07$, preserving the comparison order. The application checks cover the estimator, fallback and converged material balances. The comparison table reports current Node planning times; these machine-dependent times cover planning rather than all initialization work.

6.6 Technology in Practice

Figure 6.5 draws the loops of Section 6.4 with the hardware of a real unit in place of the schematic's symbols.

What Measures It

The oxygen loop reads the cycle gas oxygen from an analyzer, and the ethylene and carbon dioxide loops read theirs the same way. The selectivity reaches the chloride loop only once every 30 min, from an analyzer of the kind that suffers from large measurement delays and high investment and maintenance costs [13]. The hot spot that drives the override is the model's hottest cell, read with no thermocouple lag, while Figure 6.3 shows the outlet thermocouple reading 291.0 against a hot spot of 295.4 °C.

> **TECHNOLOGY** **Sensor: A Paramagnetic Oxygen Analyzer**
>
> No other industrial gas is nearly as paramagnetic as oxygen, so an analyzer that senses the pull of a magnetic field on its sample reads oxygen and ignores the rest. Nitric oxide is one of the few gases that interfere [14]. The classic design, a small dumbbell hung in the field, answers in 3 to 10 seconds, set mainly by how fast the gas in the cell is exchanged, and it is sensitive to vibration [15]. A span check above the oxygen of air needs pure oxygen as its standard, and an analyzer system needs much more maintenance than other instruments [14].

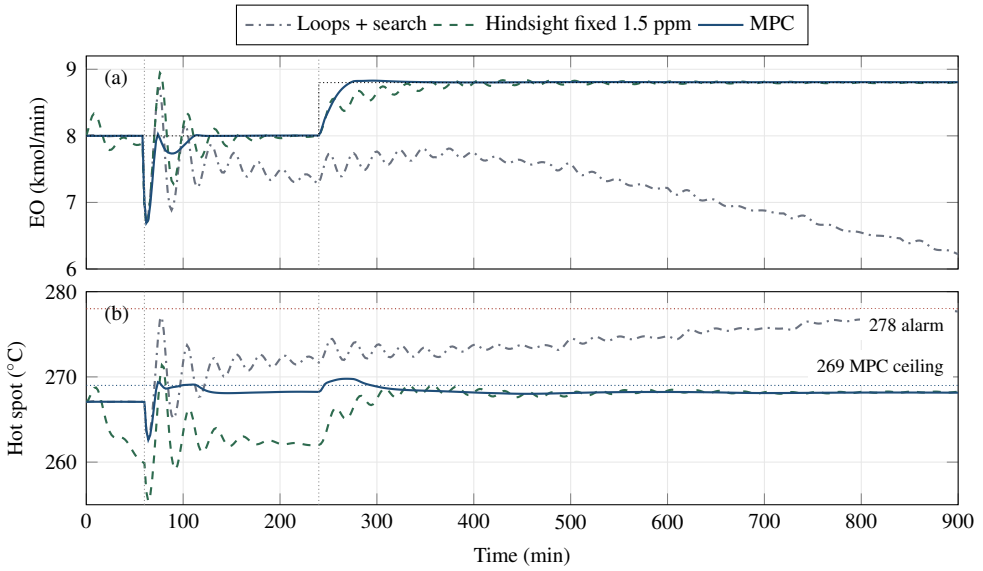


Figure 6.4 Full-duration aging and rate-request comparison: loops with the chloride search (dash-dotted), hindsight fixed 1.5 ppm (dashed) and MPC (solid). Activity falls at 60 min and the request rises at 240 min (vertical dotted lines). The upper dotted line in (a) is the requested rate, and the dotted lines in (b) are the labeled alarm and MPC ceiling. MPC and hindsight fixed 1.5 ppm produce 7706.8 and 7689.2 kmol, with mean margin indices 2.338954 and 2.340378. The fixed comparator uses a disclosed six-setting hindsight sweep and switches after the first 0.01 min physics step. MPC has worse oxygen IAE, 76.053 versus 35.108 mol%·min. No shown run exceeds the alarm.

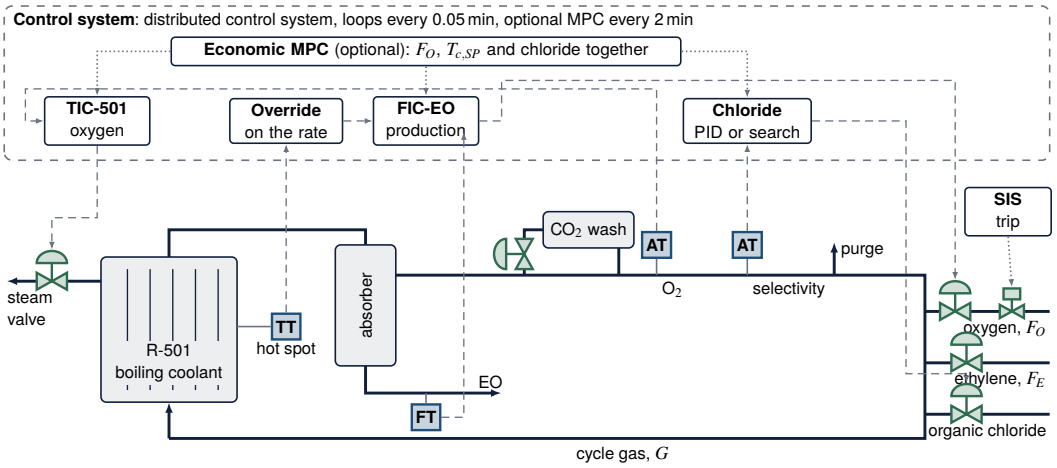


Figure 6.5 The reactor's main loops with their hardware. Tagged boxes are sensors, valve symbols final elements, dashed arrows signals and dotted ones the optional MPC and the trip. The steam valve sets the boiling pressure and so T_c. Notice that the hot spot reaches the oxygen valve only through the production setpoint. The ethylene and carbon dioxide loops, the trip's sensors, the stripper and the compressor are left out. Not to scale.

What Moves It

Five final elements act on the loop. The oxygen feed valve carries the production loop and the override. The coolant is boiling on the shell, where the reaction heat is removed and recovered by

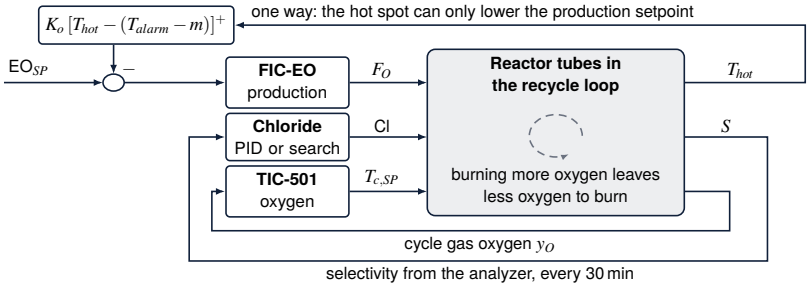


Figure 6.6 The regulatory structure as blocks. The hot spot can only lower the production setpoint, through the one-way trim of Equation (6.9). Notice the dashed loop inside the plant: the recycle's own feedback. The ethylene and carbon dioxide loops and the optional MPC are left out.

raising steam [5], and the boiling temperature of a liquid is a function of the absolute pressure it experiences [14], so the coolant setpoint $T_{c,SP}$ is in practice a pressure on the boiling side. The wash slipstream passes through a hot potassium carbonate absorber and returns to the recycle gas, and the chloride is an organic compound, typically ethyl chloride or dichloroethane, dosed into the recycle gas [5]. The model caps the wash when the column loses circulation, as in scenario 11.

> **TECHNOLOGY** **Final Element: The Oxygen Feed Control Valve**
>
> An industry code for oxygen piping counts process control valves as the most severe class of service in gaseous oxygen. They throttle at a high differential pressure, with fast, turbulent flow striking the trim, the body and at least eight valve diameters of the pipe downstream. Such valves are generally globe, modified ball, eccentric plug or butterfly types. In an oxygen system the oxygen is the oxidizer, the metals, seals, lubricants and any particles or oils are the fuel, and particle impact, compression heating and friction are the ignition sources. The design answers with burn-resistant alloys where ignition can occur and with cleaning for oxygen service [16].

Where the Controller Runs

A distributed control system holds loops like these at a supervisory level that sends set points to field controllers, with loops nested or cascading and cycle times from milliseconds to minutes [17]. The override is a selection in which only one controller output at a time acts on the process [14], here the lower of the operator's production setpoint and the one the hot spot allows. The trip belongs to a safety instrumented system with its own sensors and a logic solver separate from the regular controls, whose final elements are on/off valves or solenoids that force a control valve shut [14]. In the app every loop scans each 0.05 min in velocity form, the chloride search moves once a dwell, and the economic MPC sits above the loops and plans every 2 min. Figure 6.6 draws the same structure as blocks, with the recycle as the slow feedback inside the plant.

IN PRACTICE **Methane Ballast and a Lost Coolant**

Every site that answered the survey behind the European reference document dilutes its recycle gas with methane. Against nitrogen, methane allows more oxygen, limits the temperature rise better, needs less energy to compress and lets the purge be burned as fuel, and nitrogen serves only for a limited time when methane is short. A purge of about 0.1 to 0.2 percent of the recycle gas keeps ethane, argon and nitrogen from building up. The document lists a lost coolant supply among the abnormal events: the reactor overheats, may run away, and its pressure relief system must then act [5]. The trip in this chapter forces the feeds to zero and the wash to full instead.

What Is Modernizing It

Model predictive control has a solid foundation in refining and petrochemicals [10], and the economic version of this chapter prices production and selectivity instead of setpoint errors. Soft sensors estimate quality between analyzer reports and are also used to validate online analyzers [13], which would let a chloride search judge a step sooner than the half-hourly selectivity allows. Paramagnetic sensors built as microelectromechanical devices answer faster because their small dead volumes exchange the gas quickly [15], and a laser analyzer tuned to a single absorption line tells one compound from another even where their absorption bands overlap [14].

6.7 Limitations

One tube stands for the whole bundle, so the tube-to-tube distribution that determines where a real runaway starts is absent.

Twelve axial cells understate the true peak, and a real profile is sharper than twelve cells can render [6].

The chloride model is a fitted shape with a single lag, and real chloride has a memory of days and depends on the carrier [4]. The reader does not learn here how long a chloride change actually takes to settle on a plant.

The flammability correlation is linear in two compositions and clamped outside the range it was fitted in. The clamp is honest and it means the application cannot be used to explore compositions far from design [8].

The gas loop is one well stirred tank, so the transport delays that every composition loop on a real plant contends with are absent.

The optional economic MPC uses nominal local slopes rather than the full nonlinear industrial optimization problem [10]. Its model omits ignition curvature, analyzer lags, hot-spot migration and direct nonlinear activity effects on the EO/selectivity map. Estimated activity is a disturbance coordinate, not a calibrated catalyst measurement. The shared slacks and finite horizon provide no invariance proof. Wash failure and the suggested challenge demonstrate that prediction correction does not remove an economic tracking trade-off.

OPEN CHALLENGE **Why Chloride and Rhenium Work**

The high-selectivity catalysts of industry carry rhenium and alkali promoters on the silver, and an organic chloride dosed in the feed blocks sites on its surface. How the promoters act is still argued. A 2025 study calls the mechanism of rhenium promotion a topic of debate and finds a clear understanding of its effect limited [1]. A 2024 study finds a systematic picture of the oxygen on working silver still lacking, and essential to understanding the promoters [18]. Progress would be a mechanistic model that predicts where the chloride optimum sits and how it moves as a charge ages, in place of the fitted curve of this chapter.

6.8 Discussion

Three results generalize past epoxidation.

The first is that a minority reaction can own the energy balance. Thirteen percent of the ethylene makes sixty-five percent of the heat, and any process with a large disparity in heats of reaction deserves the same arithmetic before its cooling is designed.

The second is that a fixed-sign controller cannot hold an optimum, and the failure is conditional rather than absolute. The same loop settles from one side and walks to a trip from the other, and the condition is invisible from inside the loop. Where an objective has a maximum the first question is not how to optimize it but whether there is a measurement that is zero there [19]. Volume 11, Chapter 13 holds such an optimum with an ordinary PI loop, because its analyzer measures a difference that is zero at the peak and signed on either side. Volume 7, Chapter 4 regulates at the peak of a friction curve, where the process gain also passes through zero and reverses. Where there is no such measurement, the shipped Loops structure uses a search, and the resolution of that search is the noise on the objective divided by the product of the curvature and the step.

The third is that two constraints conflicting on one handle is a design finding rather than a tuning problem. Cooling this reactor helps the catalyst and hurts the flammability margin, and no setting of the coolant valve satisfies both. The move that relieves both constraints is the one that gives up the objective, and recognizing that early is what separates an override structure that works from a selector that oscillates.

6.9 Conclusion

An ethylene oxide reactor at 87.2 % selectivity makes 65 % of its 40 MW of heat with the 12.8 % of the ethylene that burns, which is why it is nine thousand narrow tubes in boiling water. In the simulated reactor of this chapter the peak goes from 267.0 °C at the design coolant temperature to 290.1 °C four degrees higher and has no cool solution above 248.97 °C, a total margin of 4.2 °C. The recycle loop stabilizes a thirty-five percent activity step that would ignite a once-through tube, settling the peak back at 267.6 °C on 5.68 mol% oxygen, and it overshoots to 286.6 °C on the way because the tube answers in a minute and the loop turns over in eight. The chloride optimum near 2.5 ppm is flat in selectivity, worth less than half a point across a part per million either side, and steep in hot spot, worth 22.6 °C across the same range, and an identical PID controller creeps toward its setpoint from 1.50 ppm and trips the reactor from 3.30 ppm at 381.8 min. The economic MPC reaches a 269.783 °C peak versus 271.529 for the best tested fixed-chloride policy, with nearly tied mean margins of 2.338943 and 2.340381 and larger oxygen IAE, 76.098 versus 35.081 mol%·min. A fuller model would add a tube-to-tube distribution so that a runaway can start where a real one starts, a finer axial grid, a chloride model with the memory a real catalyst has, and a transport delay in the recycle loop. The reactor shows where feedback stops being the right tool.

KEY POINTS

- The reaction nobody wants owns the heat: the eighth of the ethylene that burns makes about two thirds of the reactor's heat.
- The cool steady state ends 4.2 °C above the design coolant, and the recycle loop keeps the reactor off that cliff, but late enough to overshoot to 286.6 °C.
- The chloride optimum near 2.5 ppm is flat in selectivity and steep in hot spot, and one PID settles from below it and trips the reactor from above it.
- Cooling helps the hot spot and hurts the flammability margin, so the override cuts the production rate.

Where else this applies. Holding a peak where the process gain changes sign is also the problem of Volume 7, Chapter 4 and Volume 11, Chapter 13, and a one-way override on a hard limit guards Volume 4, Chapter 2 and Volume 4, Chapter 6.

References

[1] C. J. Keijzer, P. T. Weide, K. H. Helfferich, J. Zieciak, M. de Ridder, R. Dalebout, T. L. Lohr, J. R. Lockemeyer, P. van den Brink, and P. E. de Jongh, "Insight into the influence of Re and Cl on Ag catalysts in ethylene epoxidation," *Catalysis Science & Technology*, vol. 15, no. 2, pp. 323–333, 2025.

[2] R. J. van Welsenaere and G. F. Froment, "Parametric sensitivity and runaway in fixed bed catalytic reactors," *Chemical Engineering Science*, vol. 25, no. 10, pp. 1503–1516, 1970.

[3] M. Morbidelli and A. Varma, "Parametric sensitivity and runaway in fixed-bed catalytic reactors," *Chemical Engineering Science*, vol. 41, no. 4, pp. 1063–1071, 1986.

[4] D. Ren, H. Xu, J. Li, J. Li, and D. Cheng, "Origin of enhanced ethylene oxide selectivity by cs-promoted silver catalyst," *Molecular Catalysis*, vol. 441, pp. 92–99, 2017.

[5] H. Falcke, S. Holbrook, I. Clenahan, A. López Carretero, T. Sanalan, T. Brinkmann, J. Roth, B. Zerger, S. Roudier, and L. Delgado Sancho, "Best available techniques (BAT) reference document for the production of large volume organic chemicals," Publications Office of the European Union, Luxembourg, EUR 28882 EN, 2017.

[6] Z. Nawaz, "Heterogeneous reactor modeling of an industrial multitubular packed-bed ethylene oxide reactor," *Chemical Engineering and Technology*, vol. 39, no. 10, pp. 1845–1857, 2016.

[7] A. Kummer and T. Varga, "What do we know already about reactor runaway? a review," *Process Safety and Environmental Protection*, vol. 147, pp. 460–476, 2021.

[8] A. Pekalski and H. Pasman, "Distinction between the upper explosion limit and the lower cool flame limit in determination of flammability limit at elevated conditions," *Process Safety and Environmental Protection*, vol. 87, no. 1, pp. 47–52, 2009.

[9] L. G. Britton and B. K. Harrison, "Using chetah to estimate lower flammable limit, minimum ignition energy, and other flammability parameters," *Process Safety Progress*, vol. 33, no. 4, pp. 314–328, 2014.

[10] S. J. Qin and T. A. Badgwell, "A survey of industrial model predictive control technology," *Control Engineering Practice*, vol. 11, no. 7, pp. 733–764, 2003.

[11] D. Q. Mayne, J. B. Rawlings, C. V. Rao, and P. O. M. Scokaert, "Constrained model predictive control: Stability and optimality," *Automatica*, vol. 36, no. 6, pp. 789–814, 2000.

[12] G. Pannocchia and J. B. Rawlings, "Disturbance models for offset-free model-predictive control," *AIChE Journal*, vol. 49, no. 2, pp. 426–437, 2003.

[13] M. Kano and K. Fujiwara, "Virtual sensing technology in process industries: Trends and challenges revealed by recent industrial applications," *Journal of Chemical Engineering of Japan*, vol. 46, no. 1, pp. 1–17, 2013.

[14] T. R. Kuphaldt, *Lessons in Industrial Instrumentation*, version 2.33 ed. Open textbook, Creative Commons Attribution 4.0 license, ibiblio.org/kuphaldt/socratic/sinst, 2024.

[15] K. Jasek, M. Pasternak, and M. Grabka, "Paramagnetic sensors for the determination of oxygen concentration in gas mixtures," *ACS Sensors*, vol. 7, no. 11, pp. 3228–3242, 2022.

[16] European Industrial Gases Association, "Oxygen pipeline and piping systems," European Industrial Gases Association, Brussels, EIGA Doc 13/20, 2020.

[17] K. Stouffer, M. Pease, C. Tang, T. Zimmerman, V. Pillitteri, S. Lightman, A. Hahn, S. Saravia, A. Sherule, and M. Thompson, "Guide to operational technology (OT) security," National Institute of Standards and Technology, Gaithersburg, MD, Special Publication 800-82r3, 2023.

[18] M. Guo, N. Dongfang, M. Iannuzzi, J. A. van Bokhoven, and L. Artiglia, "Structure and reactivity of active oxygen species on silver surfaces for ethylene epoxidation," *ACS Catalysis*, vol. 14, no. 13, pp. 10 234–10 244, 2024.

[19] P. Kadlec, B. Gabrys, and S. Strandt, "Data-driven soft sensors in the process industry," *Computers & Chemical Engineering*, vol. 33, no. 4, pp. 795–814, 2009.

6.10 Exercises

6.1 Concept check · 2 min

At 87.2 % selectivity the combustion makes 65 % of the heat. Why does the heat released in a cell of this tube rise faster with temperature than the epoxidation rate alone would suggest?

(a) The epoxidation releases more heat per mole as the catalyst warms

(b) The carbon dioxide made by the combustion inhibits both reactions less when hot

(c) The cycle gas carries less heat out of a cell as its oxygen is consumed

(d) The combustion has the larger activation temperature and 12.6 times the heat

6.2 Concept check · 2 min

Scenarios 7 and 8 run the same chloride PID with the same tuning and the same 87.15 % setpoint. Started at 3.30 ppm it trips the reactor at 381.8 min. Started at 1.50 ppm it creeps toward 2.1 ppm. What distinguishes the two runs?

(a) The sign of the gain from chloride to selectivity, which reverses near 2.5 ppm

(b) The integral time, which is too short for the chloride uptake from the higher start

(c) The hot spot override, which acts in scenario 8 and is switched off in scenario 7

(d) The analyzer cycle, which reports the selectivity too late when the chloride is high

6.3 Concept check · 2 min

The hot spot is above the start of its override. Why does the override cut the production setpoint instead of lowering the coolant temperature?

(a) The coolant drum answers too slowly to reach the hot spot before the alarm

(b) A cooler reactor leaves more unreacted oxygen and walks the loop toward flammability

(c) Lowering the coolant cuts production at once, and the override exists to keep it

(d) The coolant has no lasting effect on the hot spot once the recycle has settled

6.4 Theory and calculation · 6 min

The reactor makes 8.00 kmol/min of ethylene oxide at 87.21 % selectivity, with $\Delta H_1 = 105\,\mathrm{kJ/mol}$ and $\Delta H_2 = 1327\,\mathrm{kJ/mol}$ per mole of ethylene.

(a) Find the fraction of the heat made by the combustion. *Checkpoint:* 65.0 %.

(b) Find the ethylene burned in kmol/min and the total duty in MW. *Checkpoint:* 1.173 kmol/min, 39.95 MW.

(c) Use Equation (1.5) with $E_1/R = 8200\,\mathrm{K}$ and $E_2/R = 11\,800\,\mathrm{K}$ to find the effective activation of the heat generated. Taking each quantity to grow by $(E/R)/T^2$ per kelvin, compare the growth of the heat and of the epoxidation rate at the 267.1 °C hot spot. *Checkpoint:* 10 540 K, then 3.61 % and 2.81 % per kelvin.

6.5 Theory and calculation · 7 min

At the design point the oxygen feed is $F_O = 7.606\,\text{kmol/min}$, the purge $P = 1.20\,\text{kmol/min}$ and the cycle gas oxygen 7.20 mol%, with 8.00 kmol/min of ethylene oxide at 87.21 % selectivity. Each mole of ethylene oxide uses half a mole of oxygen and each mole of ethylene burned uses three.

(a) Use Equation (6.8) to find the oxygen reacted, and check it against the stoichiometry. Find the oxygen used per mole of product. *Checkpoint:* 7.520 kmol/min and 0.940.

(b) In scenario 2, with the oxygen feed fixed, two degrees of extra coolant bring the Selectivity tile to 86.92 % and the cycle gas oxygen to 6.80 mol%. Find the production the oxygen balance allows. *Checkpoint:* 7.91 kmol/min.

(c) Find the production gained per kmol/min of extra oxygen feed at constant selectivity, and the time the loop takes to turn over once (holdup 2450 kmol, circulation 320 kmol/min). Use them to explain the rise of production to 8.43 kmol/min within eight minutes of the coolant step and its fall afterward. *Checkpoint:* 1.064 and 7.66 min.

6.6 Theory and calculation · 6 min

The step and search optimizer of scenario 9 moves the chloride by $h = 0.3$ ppm and ignores selectivity differences under $\sigma = 0.04$ %. Near the maximum the selectivity curve has a curvature $|S''| = 0.7$ % per ppm^2.

(a) Find the distance from the top inside which a step cannot be told apart, $d = \sigma / (|S''|\,h)$. *Checkpoint:* 0.19 ppm.

(b) Repeat with 0.5 % of analyzer noise in place of σ. *Checkpoint:* 2.38 ppm.

(c) Taking $\Delta S = \tfrac{1}{2}|S''|d^2$, find what being 0.5 ppm from the top costs, and compare it with the measured hunt, which averages 87.16 % against 87.21 at the peak. Then find the step that would resolve 0.1 ppm at $\sigma = 0.04$ % and say what it would do to the hunt. *Checkpoint:* 0.09 points against 0.05, and 0.57 ppm.

6.7 App challenge · 8 min

Load scenario 5, "5 · The recycle is the real stabilizer", at the default seed. It starts with the Oxygen concentration loop in Manual and the Hot spot override Off, and the catalyst activity steps to 1.35 at 20 min. Run at speed 20 (20 min per wall-clock second) until the clock passes 240 min, pause and export the CSV. A run longer than an hour exports its time column as Time (h), in hours, so convert each time below from minutes.

(a) Find the largest `hot_C` and its time, and read `metric_alarm_min`, the minutes above the 278 °C alarm, in the row at 240.0 min. *Checkpoint:* 286.6 °C at 25.9 min, then 6.9 min.

(b) In the row at 240.0 min, read `hot_C`, `o2_pct` and `o2_cmd`, and say what stopped the tube. *Checkpoint:* 267.6 °C, 5.68 mol%, 7.592 kmol/min.

(c) Press Reset, set Hot spot override to On before Run, run again to 240 min and repeat (a). Explain why the override helps so little. *Checkpoint:* 283.2 °C at 24.9 min, then 4.6 min.

6.8 App challenge · 8 min

Load scenario 10, "10 · Two margins, opposite directions", at the default seed. The Production and Oxygen concentration loops start in Manual, and the coolant steps to 241.0 °C at 20 min and to 248.8 °C at 220 min. Run at speed 60 (60 min per wall-clock second) until the clock passes 480 min, pause and export the CSV. A run longer than an hour exports its time column as Time (h), in hours, so convert each time below from minutes.

(a) Read `hot_C` and `o2_margin_pct` in the rows at 220.0 and 480.0 min. *Checkpoint:* 262.8 and 0.52, then 271.6 and 2.18.

(b) Find the largest `hot_C` after 220 min and its time, and read `metric_alarm_min` at 480.0 min. *Checkpoint:* 286.4 °C at 231.3 min, then 10.4 min.

(c) Switch both loops to Auto and Hot spot override to On, run another hour, export again and count the minutes with `override_active` equal to 1 after the switch. Explain what moved each margin back. *Checkpoint:* 6 min.

6.9 App challenge · 10 min

Load the challenge, "Challenge · a shift on a fresh charge", at its default seed. For each run below, run at speed 60 (60 min per wall-clock second) until the clock passes 900 min, about 15 s, pause and export the CSV. A run longer than an hour exports its time column as Time (h), in hours, so convert each time below from minutes. The graded number is the worst $|\texttt{o2_pct} - \texttt{o2_sp_pct}|$ over the rows from 594 min, which the progress panel also reports as the worst oxygen error. Read `o2_margin_pct` in the row at 900.0 min.

(a) Run the case as loaded. *Checkpoint:* 0.314 mol%, margin 1.73 mol%.

(b) Press Reset, set Oxygen loop gain to 7.0 and Oxygen integral time to 18.0 min before Run, change nothing else, and run again. *Checkpoint:* 0.077 mol%, margin 1.56 mol%.

(c) Press the reload button beside the scenario list, press Reveal suggested tuning and run again. Say why the suggestion is worth having although its graded number is worse than in (b). *Checkpoint:* 0.105 mol%, margin 1.75 mol%.

6.10 Application area · 3 min

A plant engineer proposes running the carbonate wash harder, taking the cycle gas carbon dioxide from 5.00 to 4.00 mol% to gain catalyst activity. Show Model lists the coefficients of Equation (6.7), the limiting oxygen lost per mol% of ethylene and gained per mol% of carbon dioxide, as $a = 0.115$ and $b = 0.180$. Find the new limit of flammability and the margin at 7.20 mol% oxygen and 24.0 mol% ethylene, and the gain in rate from the inhibition term $\phi = 1/(1 + 4.6\,y_C)$. What does the oxygen loop do with the gain?

6.11 Application area · 4 min

An operations engineer wants to set a coolant temperature ceiling on a real reactor from the 248.97 °C at which the cool state of this tube ends. Apply Equation (1.13) with a coolant loop that swings 0.5 °C, no measurement error and 1 °C of reserve. Then name two simplifications of the model that make the real margin smaller than the simulator's 4.2 °C.

6.12 Review the agent · 5 min

An AI assistant reviewing scenario 7 writes: "The trip at 381.8 min is a tuning problem. A chloride PID gain of 1.20 ppm per percent is aggressive for a loop behind a 55 min uptake and a 30 min analyzer. Cut Chloride PID gain to 0.30 and the loop will settle at its 87.15 % setpoint from 3.30 ppm, as it does from 1.50 ppm in scenario 8." Find the flaw, and say how you would check it in the app.