COMSOL MULTIPHYSICS®

Startup of a CSTR

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Startup of a CSTR

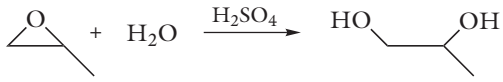
Introduction

The hydrolysis of propylene oxide into propylene glycol is an important chemical process with 400,000 metric tons produced worldwide each year. Propylene glycol finds wide application as a moisturizer in foods, pharmaceuticals, and cosmetics.

In this example you model the startup phase of a continuous stirred tank reactor (CSTR) used to produce propylene glycol. The nonisothermal process is described by a set of coupled mass and energy balances that you easily set up and solve in the Reaction Engineering Lab. The model highlights the use of the predefined CSTR reactor type and also shows how to enter the thermodynamic data needed for energy balances.

Model Description

This model reproduces the results found in Ref. 1. Propylene glycol (PrOH) is produced from the reaction of propylene oxide (PrO) with water (W) in the presence of an acid catalyst:



(1)

The reaction rate (mol/(m^3·s)) is first order with respect to propylene oxide:

$$r_1 = -k_1 c_{\mathrm{PrO}} \tag{2}$$

where the rate constant is temperature dependent according to the expression

$$k_1 = A_1 \exp\left(-\frac{E_1}{\mathrm{Rg}T}\right) \tag{3}$$

The Arrhenius parameters in Equation 3 are $A_1 = 4.71 \cdot 10^9$ (1/s) and $E_1 = 75{,}358$ (J/mol).

The liquid phase reaction takes place in a continuous stirred tank reactor (CSTR) equipped with a heat-exchanger. Methanol (MeOH) is added to the mixture but does not react. It is further assumed that the mixture density is constant over time.

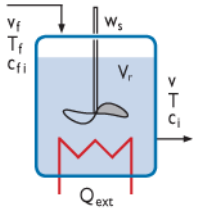


Figure 1: A perfectly mixed CSTR for the production of propylene glycol. The CSTR is a predefined reactor type in the Reaction Engineering Lab.

The time evolution of the nonisothermal reacting system is given by several coupled balance equations.

The species mass balances are

$$\frac{d(c_i V_r)}{dt} = v_{f,i}\, c_{f,i} - v c_i + R_i V_r \tag{4}$$

In Equation 4, c_i is the species molar concentration (mol/m^3), V_r denotes the reactor volume (m^3), R_i is the species rate expression (mol/(m^3·s)), and v is the volumetric flow rate (m^3/s).

For an incompressible and ideally mixed reacting liquid, the energy balance is

$$V_r \sum_i c_i C_{p,i} \frac{dT}{dt} = Q + Q_{\text{ext}} + \sum_i v_{f,i}\, c_{f,i} (h_{f,i} - h_i) \tag{5}$$

where $C_{p,i}$ is the species molar heat capacity (J/(mol·K)), and T is the temperature (K). On the right-hand side, Q represents the heat due to chemical reaction (J/s), and Q_{ext} denotes heat added to the system (J/s), for instance by a heat exchanger. The last term signifies heat added as species flow through the reactor. In this term, h_i is the species molar enthalpy (J/mol).

This example assumes that the species heat capacities, $C_{p,i}$, represent an average over the temperature interval. The associated species' enthalpies are then given by

$$h_i = C_{p,i}(T - T_{\text{ref}}) + h_i(T_{\text{ref}}) \tag{6}$$

where $h_i(T_{\text{ref}})$ is the standard heat of formation at the reference temperature T_{ref}.

The heat of reaction is given by

$$Q = -V_r \sum_j H_j r_j \tag{7}$$

where H_j is the enthalpy of reaction (J/mol), and r_j denotes the reaction rate (mol/(m^3·s)).

The heat added by the heat exchanger is given by

$$Q_{\text{ext}} = F_x C_{p,x}(T_x - T) \cdot \left[1 - \exp\left(\frac{UA}{F_x C_{p,x}}\right)\right] \tag{8}$$

where F is the molar flow rate (mol/s), U is the overall heat transfer coefficient (J/(K·m^2·s)), and A represents the heat exchange area (m^2). The subscript x refers to the heat exchanger medium, which in this case is water. T_x is the inlet temperature of the heat exchanger medium.

The following table summarizes additional parameters describing the reactor setup and process conditions:

PARAMETER	VALUE	DESCRIPTION
V_r	1.89 m^3	Reactor volume
v_f	3.47·10^{-3} m^3/s	Volumetric flow rate
$c_{f,PrO}$	2903 mol/m^3	Concentration of PrO in feed stream
$c_{f,W}$	36291 mol/m^3	Concentration of W in feed stream
$c_{f,MeOH}$	3629 mol/m^3	Concentration of MeOH in feed stream
$c_{0,W}$	55273 mol/m^3	Initial concentration of W in the reactor
$C_{p,PrO}$	146.5 J/(mol·K)	Heat capacity of PrO
$C_{p,W}$	75.4 J/(mol·K)	Heat capacity of W
$C_{p,PrOH}$	192.6 J/(mol·K)	Heat capacity of PrOH
$C_{p,MeOH}$	81.6 J/(mol·K)	Heat capacity of MeOH
C_{px}	75.4 J/(mol·K)	Heat capacity of heat exchanger medium
$h_{ref,PrO}$	-153.5·10^3 J/mol	Enthalpy of formation of PrO at T_{ref}
$h_{ref,W}$	-286.1·10^3 J/mol	Enthalpy of formation of W at T_{ref}
$h_{ref,PrOH}$	-525.6·10^3 J/mol	Enthalpy of formation of PrOH at T_{ref}
$h_{ref,MeOH}$	-238.6 J/mol	Enthalpy of formation of MeOH at T_{ref}
T_f	297 K	Feed stream temperature

PARAMETER	VALUE	DESCRIPTION
T_0	297 K	Initial reactor temperature
T_{ref}	293 K	Reference temperature
T_x	289 K	Temperature of heat exchanger medium at inlet
F_x	126 mol/s	Heat exchanger medium molar flow
UA	8441 J/(s·K)	Heat exchange parameter

The model described here is readily set up and solved using the predefined CSTR reactor type in the Reaction Engineering Lab.

Results

Figure 2 shows the concentration of PrO (mol/m^3) and the reactor temperature (K) as a function of reaction time.

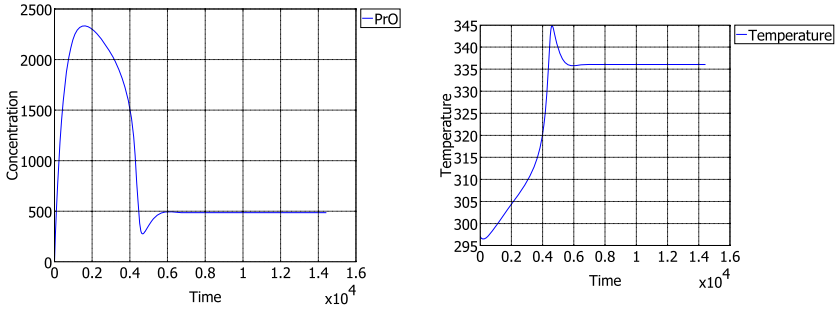


Figure 2: Concentrations of reactant PrO (mol/m^3) after 4 hours of operation (left) and reactor temperature (K) after 4 hours of operation (right).

Initially both the reactant concentration and the temperature oscillate around their respective steady-state values (491 mol/m^3 and 336 K, respectively). The same result

can be illustrated by a trajectory in the concentration-temperature phase plane as presented in Figure 3.

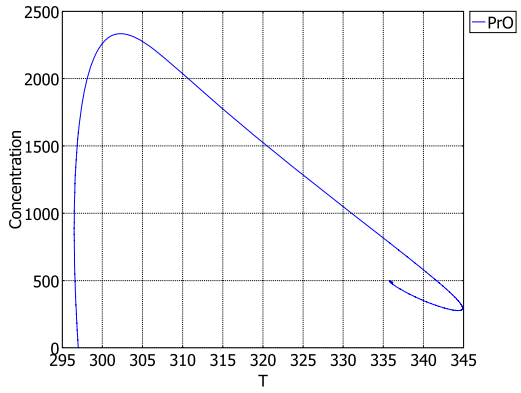


Figure 3: Trajectory in the concentration-temperature phase plane.

The model predicts that the reactor temperature passes a maximum value higher than the steady-state temperature. From a safety perspective it is therefore relevant to look closer at possible sets of initial conditions to see if process operation limits are violated. In the process modeled here, it is undesirable to exceed a reactor temperature of 355 K to avoid undesirable side reactions and not damage reactor equipment. Figure 4 shows the concentration-temperature phase plane for three initial condition sets: ($c_{\mathrm{PrO}} = 0$, $T_0 = 297$ K), ($c_{\mathrm{PrO}} = 0$, $T_0 = 340$ K), and ($c_{\mathrm{PrO}} = 1400$, $T_0 = 340$ K).

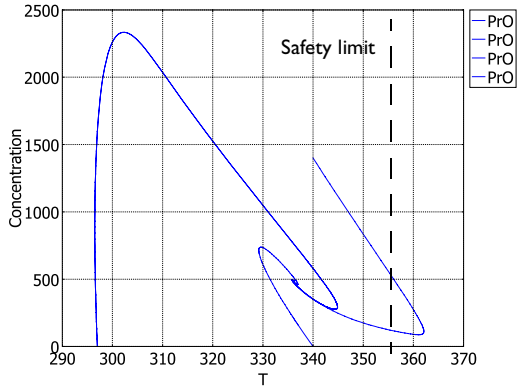


Figure 4: Trajectories in the concentration-temperature phase plane for three sets of initial conditions.

The plot shows that all investigated initial conditions converge to the same steady state. However, starting with $c_{PrO} = 1400$ mol/m^3 and $T_0 = 340$ K leads to violation of the temperature safety limits.

Reference

1. H. S. Fogler, *Elements of Chemical Reaction Engineering 3rd Ed.*, Prentice Hall PTR, 1999, Example 9-4, pp. 553–559.