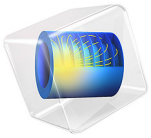


Model created in COMSOL Multiphysics 6.4

Startup of a Continuous Stirred Tank Reactor

Introduction

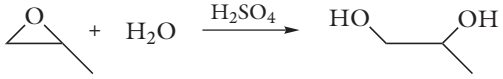
The hydrolysis of propylene oxide into propylene glycol is an important chemical process with 400,000 metric tons produced worldwide each year. Propylene glycol finds wide application as a moisturizer in foods, pharmaceuticals, and cosmetics.

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

This example reproduces results found in Ref. 1.

Model Description

Propylene glycol ($C_3H_8O_2$) is produced from the reaction of propylene oxide (C_3H_6O) with water (H_2O) in the presence of an acid catalyst:



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

$$r_1 = k_1 c_{C3H6O}$$

where the rate constant is temperature dependent according to the Arrhenius expression:

$$k_1 = A_1 \exp\left(-\frac{E_1}{R_g T}\right) \tag{1}$$

The Arrhenius parameters in Equation 1 are $A_1 = 4.71 \cdot 10^9$ s^{-1} and $E_1 = 75.358$ kJ/mol.

The liquid phase reaction takes place in a continuous stirred tank reactor (CSTR) equipped with a heat-exchanger. Methanol (CH_3OH) is also added to the mixture but does not react. It is further assumed that the reactor volume is constant over time.

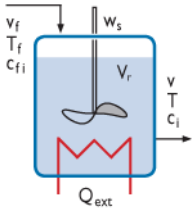


Figure 1: A perfectly mixed CSTR for the production of propylene glycol. The CSTR is a predefined reactor type in the Chemical Reaction Engineering Module.

The time evolution of the nonisothermal reacting system is given by several coupled balance equations. The species mass balances are:

$$V_{\mathrm{r}}\frac{\mathrm{d}c_i}{\mathrm{d}t} = v_{\mathrm{f}}\,c_{\mathrm{f},i} - vc_i + R_i V_{\mathrm{r}} \tag{2}$$

In Equation 2, c_i is the species molar concentration (SI unit: mol/m^3), V_{r} denotes the reactor volume (SI unit: m^3), R_i is the species rate expression (SI unit: mol/(m^3·s)), and v_{f} is the volumetric flow rate of the feed inlet (SI unit: m^3/s). v is the volumetric flow of the species exiting the reactor and is defined as:

$$v = v_{\mathrm{f},i} + v_{\mathrm{p}} = v_{\mathrm{f},i} + V_r\sum_i \frac{R_i M_i}{\rho_i}$$

v_{p} is the volumetric production rate, arising due to differences in molar mass, M_i, and densities, ρ_i, of the species.

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

$$V_{\mathrm{r}}\sum_i c_i C_{p,i}\frac{\mathrm{d}T}{\mathrm{d}t} = Q + Q_{\mathrm{ext}} + \sum_i v_{\mathrm{f},i}\,c_{\mathrm{f},i}(h_{\mathrm{f},i} - h_i)$$

where $C_{p,i}$ is the species molar heat capacity (SI unit: J/(mol·K)), and T is the temperature (SI unit: K). On the right-hand side, Q represents the heat due to chemical reaction (SI unit: J/s), and Q_{ext} denotes heat added to the system (SI unit: 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 (SI unit: 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:

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

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:

$$Q = -V_{\text{r}} \sum_j H_j r_j$$

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

The heat added by the heat exchanger is given by:

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

where F is the molar flow rate (SI unit: mol/s), U is the overall heat transfer coefficient (SI unit: J/(K·m^2·s)), and A represents the heat exchange area (SI unit: 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
$c_{f,C3H6O}$	2903 mol/m^3	Concentration of propylene oxide in feed stream
$c_{f,H2O}$	36291 mol/m^3	Concentration of water in feed stream
$c_{f,CH3OH}$	3629 mol/m^3	Concentration of methanol in feed stream
$c_{0,H2O}$	55273 mol/m^3	Initial concentration of water in the reactor
ρ_{C3H6O}	830 kg/m^3	Density of propylene oxide
ρ_{H2O}	1000 kg/m^3	Density of water
ρ_{C3H8O2}	1036 kg/m^3	Density of propylene glycol
ρ_{CH3OH}	792 kg/m^3	Density of methanol

PARAMETER	VALUE	DESCRIPTION
$C_{p,C3H6O}$	146.5 J/(mol·K)	Heat capacity of propylene oxide
$C_{p,H2O}$	75.4 J/(mol·K)	Heat capacity of water
$C_{p,C3H8O2}$	192.6 J/(mol·K)	Heat capacity of propylene glycol
$C_{p,CH3OH}$	81.6 J/(mol·K)	Heat capacity of methanol
C_{px}	75.4 J/(mol·K)	Heat capacity of heat exchanger medium
$h_{ref,C3H6O}$	$-153.5 \cdot 10^3$ J/mol	Enthalpy of formation of propylene oxide at T_{ref}
$h_{ref,H2O}$	$-286.1 \cdot 10^3$ J/mol	Enthalpy of formation of water at T_{ref}
$h_{ref,C3H8O2}$	$-525.6 \cdot 10^3$ J/mol	Enthalpy of formation of propylene glycol at T_{ref}
$h_{ref,CH3OH}$	-238.6 J/mol	Enthalpy of formation of methanol at T_{ref}
T_f	297 K	Feed stream temperature
T_0	340 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
U_A	8441 J/(s·K)	Heat exchange parameter

The model described here is readily set up and solved using the predefined CSTR reactor with constant volume in the Reaction Engineering interface available in the Chemical Reaction Engineering Module.

Figure 2 shows the concentration of propylene oxide (SI unit: mol/m^3) as a function of reaction time.

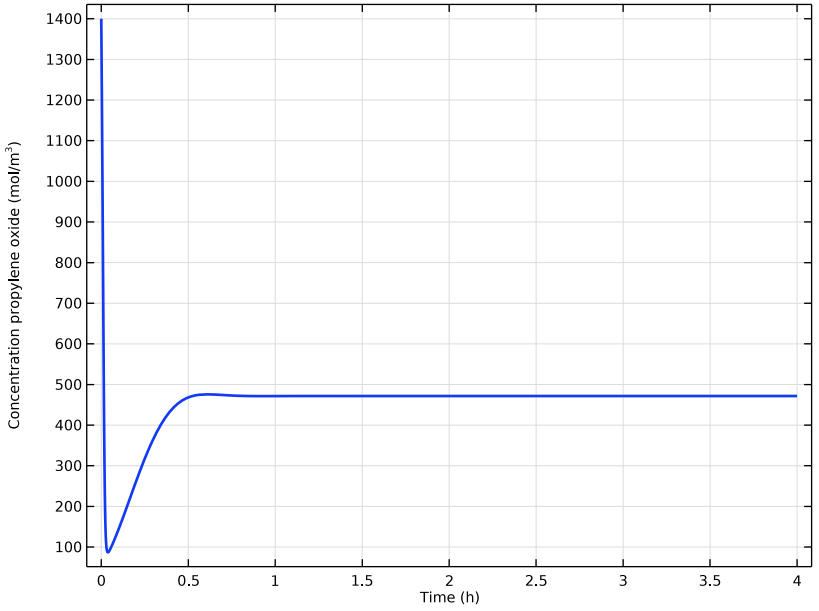


Figure 2: Concentrations of reactant propylene oxide (mol/m^3) during the first 4 hours of operation.

The corresponding development of the reactor temperature is shown in Figure 3.

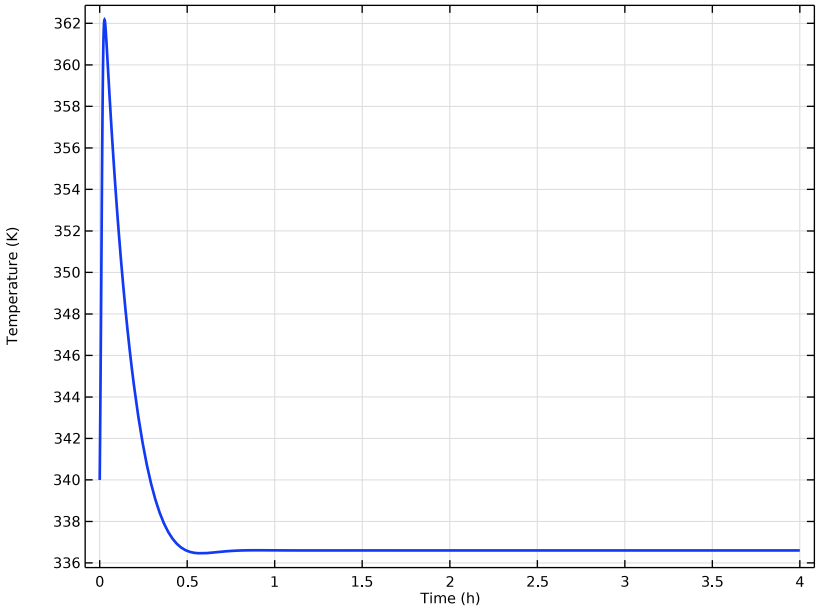


Figure 3: Reactor temperature (K) during the first 4 hours of operation.

Initially both the reactant concentration and the temperature oscillate around their respective steady-state values (472 mol/m^3 and 337 K, respectively). 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 scenarios: ($c_{C3H6O} = 0$, $T_0 = 297$ K), ($c_{C3H6O} = 0$, $T_0 = 340$ K), and ($c_{C3H6O} = 1400$, $T_0 = 340$ K).

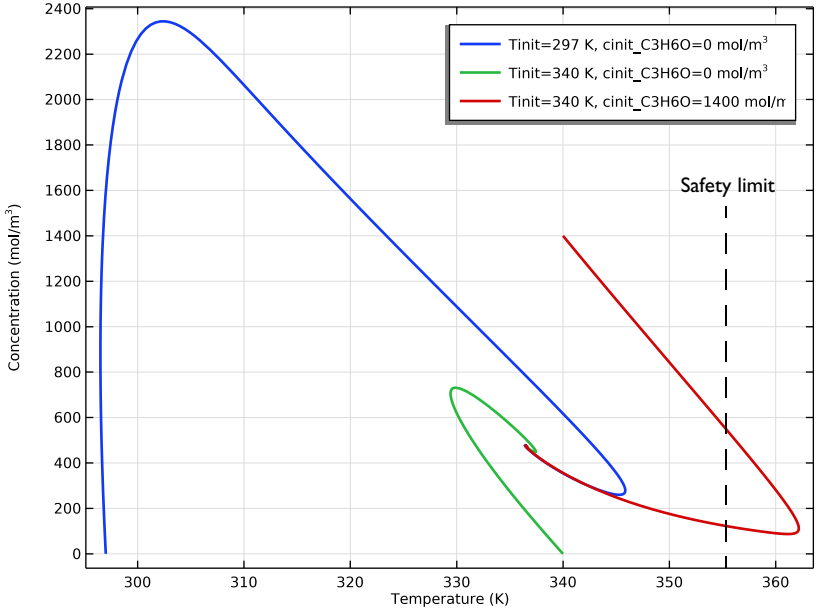


Figure 4: Trajectories in the concentration-temperature phase plane for three sets of initial conditions.

The plot shows that all investigated initial conditions converge to the same steady state. However, starting with $c_{C3H6O} = 1400$ 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, Example 9-4, pp. 553–559, 1999.

Application Library path: `Chemical_Reaction_Engineering_Module/Tutorials/cstr_startup`

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click **0D**.

2 In the **Select Physics** tree, select **Chemical Species Transport** > **Reaction Engineering (re)**.

3 Click **Add**.

4 Click **Study**.

5 In the **Select Study** tree, select **General Studies** > **Time Dependent**.

6 Click **Done**.

GLOBAL DEFINITIONS

Add a set of model parameters by importing their definitions from a data text file provided with the **Application Library**.

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

2 In the **Settings** window for **Parameters**, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `cstr_startup_parameters.txt`.

DEFINITIONS

Similarly, variables for the concentration-dependent and temperature-dependent enthalpies are available in a text file.

Variables 1

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Definitions** and choose **Variables**.

2 In the **Settings** window for **Variables**, locate the **Variables** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `cstr_startup_variables.txt`.

Select the **Reactor Type**-CSTR, constant volume for a liquid mixture and include the **Energy Balance**. That is, nonisothermal conditions apply.

REACTION ENGINEERING (RE)

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Reaction Engineering (re)**.

2 In the **Settings** window for **Reaction Engineering**, locate the **Reactor** section.

3 From the **Reactor type** list, choose **CSTR, constant volume**.

4 Locate the **Energy Balance** section. From the **Energy balance** list, choose **Include**.

5 In the Q_{ext} text field, type `Q_xch`.

6 Click to expand the **Mixture Properties** section. From the **Phase** list, choose **Liquid**.

7 Locate the **Reactor** section. Find the **Mass balance** subsection. In the V_{r} text field, type `Vr_tank`.

Reaction 1

1 In the **Reaction Engineering** toolbar, click  **Reaction**.

Add the reaction. Note that the reaction in this example is of first order in regard to propylene oxide, not the default stoichiometric reaction order.

2 In the **Settings** window for **Reaction**, locate the **Reaction Formula** section.

3 In the **Formula** text field, type `C3H6O+H2O=>C3H8O2`.

4 Locate the **Reaction Rate** section. From the list, choose **User defined**.

5 In the r_j text field, type `re.kf_1*re.c_C3H6O`.

6 Locate the **Reaction Orders** section. Find the **Volumetric overall reaction order** subsection. In the **Forward** text field, type `1`.

7 Locate the **Rate Constants** section. Select the **Use Arrhenius expressions** checkbox.

8 In the A^{f} text field, type `Af_reaction`.

9 In the E^{f} text field, type `Ea_reaction`.

Species 1

1 In the **Reaction Engineering** toolbar, click  **Species**.

2 In the **Settings** window for **Species**, locate the **Name** section.

3 In the text field, type `CH3OH`.

Species: C3H6O

1 In the **Model Builder** window, click **Species: C3H6O**.

2 In the **Settings** window for **Species**, locate the **Chemical Formula** section.

3 In the ρ text field, type `rho_C3H6O`.

Species: H2O

1 In the **Model Builder** window, click **Species: H2O**.

2 In the **Settings** window for **Species**, locate the **Chemical Formula** section.

3 In the ρ text field, type `rho_H2O`.

Species: C3H8O2

1 In the **Model Builder** window, click **Species: C3H8O2**.

2 In the **Settings** window for **Species**, locate the **Chemical Formula** section.

3 In the ρ text field, type `rho_C3H8O2`.

Species: CH3OH

1 In the **Model Builder** window, click **Species: CH3OH**.

2 In the **Settings** window for **Species**, locate the **Chemical Formula** section.

3 In the ρ text field, type `rho_CH3OH`.

Feed Inlet 1

1 In the **Reaction Engineering** toolbar, click **Feed Inlet**.

Define the inlet feed stream of the CSTR.

2 In the **Settings** window for **Feed Inlet**, locate the **Feed Inlet Properties** section.

3 In the v_f text field, type `v_feed`.

4 In the T_f text field, type `Tfeed`.

5 Locate the **Feed Inlet Concentration and Enthalpy** section. In the table, enter the following settings (clear all the checkboxes in the rightmost column):

Species	Concentration (mol/m^3)	Enthalpy	Species enthalpy (J/mol)
C3H6O	`cfeed_C3H6O`	Species enthalpy	subst(re.h_C3H6O, re.T, re.feed1.Tf)
CH3OH	`cfeed_CH3OH`	Species enthalpy	subst(re.h_CH3OH, re.T, re.feed1.Tf)
H2O	`cfeed_H2O`	Species enthalpy	subst(re.h_H2O,re.T, re.feed1.Tf)

Initial Values 1

1 In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **General Parameters** section.

3 In the T_0 text field, type `Tinit`.

4 Locate the **Volumetric Species Initial Values** section. In the table, enter the following settings:

Species	Concentration (mol/m^3)
C3H6O	cinit_C3H6O
H2O	cinit_H2O

Species: C3H6O

1 In the **Model Builder** window, click **Species: C3H6O**.

2 In the **Settings** window for **Species**, click to expand the **Thermodynamic Expressions** section.

3 From the list, choose **User defined**.

4 In the C_p text field, type cp_C3H6O.

5 In the h text field, type h_C3H6O.

Species: H2O

1 In the **Model Builder** window, click **Species: H2O**.

2 In the **Settings** window for **Species**, locate the **Thermodynamic Expressions** section.

3 From the list, choose **User defined**.

4 In the C_p text field, type cp_H2O.

5 In the h text field, type h_H2O.

Species: C3H8O2

1 In the **Model Builder** window, click **Species: C3H8O2**.

2 In the **Settings** window for **Species**, locate the **Thermodynamic Expressions** section.

3 From the list, choose **User defined**.

4 In the C_p text field, type cp_C3H8O2.

5 In the h text field, type h_C3H8O2.

Species: CH3OH

1 In the **Model Builder** window, click **Species: CH3OH**.

2 In the **Settings** window for **Species**, locate the **Thermodynamic Expressions** section.

3 From the list, choose **User defined**.

4 In the C_p text field, type cp_CH3OH.

5 In the h text field, type h_CH3OH.

STUDY 1

Step 1: Time Dependent

1 In the **Model Builder** window, under **Study 1** click **Step 1: Time Dependent**.

2 In the **Settings** window for **Time Dependent**, locate the **Study Settings** section.

3 From the **Time unit** list, choose **h**.

4 In the **Output times** text field, type `4`.

First, compute the temperature and concentrations.

5 In the **Study** toolbar, click **Compute**.

The following instructions generate Figure 2 and Figure 3.

RESULTS

Concentration (re)

1 In the **Settings** window for **1D Plot Group**, click to expand the **Title** section.

2 From the **Title type** list, choose **None**.

3 Locate the **Plot Settings** section.

4 Select the **y-axis label** checkbox. In the associated text field, type `Concentration propylene oxide (mol/m<sup>3</sup>)`.

Global 1

1 In the **Model Builder** window, expand the **Concentration (re)** node, then click **Global 1**.

2 In the **Settings** window for **Global**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Reaction Engineering** > **re.c_C3H6O - Concentration - mol/m³**.

3 Click to expand the **Coloring and Style** section. From the **Width** list, choose **2**.

4 Click to expand the **Legends** section. Clear the **Show legends** checkbox.

5 In the **Concentration (re)** toolbar, click **Plot**.

Temperature (re)

1 In the **Model Builder** window, under **Results** click **Temperature (re)**.

2 In the **Settings** window for **1D Plot Group**, locate the **Title** section.

3 From the **Title type** list, choose **None**.

Global 1

1 In the **Model Builder** window, expand the **Temperature (re)** node, then click **Global 1**.

2 In the **Settings** window for **Global**, locate the **Coloring and Style** section.

3 From the **Width** list, choose **2**.

4 Locate the **Legends** section. Clear the **Show legends** checkbox.

STUDY 1

Next, compute the corresponding solutions for a set of initial temperatures and propylene-oxide concentrations.

Parametric Sweep

1 In the **Study** toolbar, click **Parametric Sweep**.

2 In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.

3 Click **Add**.

4 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
Tinit (Initial reactor temperature)	`297[K] 340[K] 340[K]`	K

5 Click **Add**.

6 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
cinit_C3H6O (Initial concentration, propylene oxide)	`0 0 1400[mol/m^3]`	`mol/m^3`

7 In the **Study** toolbar, click **Compute**.

The following instructions generate Figure 4.

RESULTS

Concentration vs. Temperature (re)

1 In the **Settings** window for **1D Plot Group**, type `Concentration vs. Temperature (re)` in the **Label** text field.

2 Locate the **Title** section. From the **Title type** list, choose **None**.

Global 1

1 In the **Model Builder** window, expand the **Concentration vs. Temperature (re)** node, then click **Global 1**.

2 In the **Settings** window for **Global**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Reaction Engineering** > **re.c_C3H6O - Concentration - mol/m³**.

3 Click **Replace Expression** in the upper-right corner of the **x-Axis Data** section. From the menu, choose **Component 1 (comp1)** > **Reaction Engineering** > **re.T - Temperature - K**.

4 Locate the **Coloring and Style** section. From the **Width** list, choose **2**.

5 Locate the **Legends** section. Find the **Include** subsection. Clear the **Expression** checkbox.

6 Click the  **Zoom Extents** button in the **Graphics** toolbar.

7 In the **Concentration vs. Temperature (re)** toolbar, click  **Plot**.

Temperature vs. Time (re)

1 In the **Settings** window for **1D Plot Group**, type `Temperature vs. Time (re)` in the **Label** text field.

2 Click to expand the **Title** section. From the **Title type** list, choose **None**.

Global 1

1 In the **Model Builder** window, expand the **Temperature (re) 1** node, then click **Results** > **Temperature vs. Time (re)** > **Global 1**.

2 In the **Settings** window for **Global**, locate the **Coloring and Style** section.

3 From the **Width** list, choose **2**.

4 Locate the **Legends** section. Find the **Include** subsection. Clear the **Expression** checkbox.

5 In the **Temperature vs. Time (re)** toolbar, click  **Plot**.