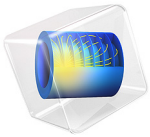

Semibatch Polymerization

Introduction

As reactant monomer converts into polymer chains, the density of the reacting mixture often changes notably. This example looks at how this effect impacts the total production of polymer in a process. The liquid phase polymerization takes place in a semibatch reactor, where two operating conditions are compared. In the first scenario, the feed of monomer to the reactor is turned off once the maximum volume capacity is reached. In a second scenario, the feed of monomer is allowed to continuously compensate for the volume change due to chemical reaction.

The model illustrates the use of the Semibatch reactor type, which is predefined in the Reaction Engineering interface in the Chemical Reaction Engineering Module. It also shows how to set timed events, in this case for controlling the reactant feed to the reactor. This example reproduces results found in Ref. 1.

Model Definition

A liquid phase polymerization can be modeled as a first order irreversible reaction:

$$\mathrm{M} \xrightarrow{k_1} \mathrm{P}$$

$$r_1 = k_1 c_M$$

In the above equations, M denotes the monomer, P the polymer, r is the reaction rate (SI unit: mol/(m^3·s)), k is the rate constant (SI unit: 1/s), and c_M is the concentration of the monomer. This process takes place in the presence of water.

The polymerization takes place in a semibatch reactor with a volume capacity of 20 m^3. Initially the reactor is charged with 10 m^3 of water. Pure monomer enters the reactor with a volumetric flow rate of v_f = 1 m^3/min.

Figure 1 shows a schematic representation of the semibatch reactor.

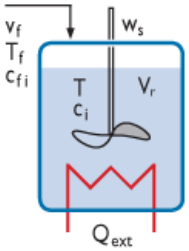

Figure 1: The Semibatch reactor is a predefined reactor type in the Reaction Engineering interface.

The following mass balance describes the semibatch reactor:

$$\frac{d(c_i V_r)}{dt} = v_{f,i}\, c_{f,i} + R_i V_r \tag{1}$$

In Equation 1, c_i is species molar concentration (SI unit: mol/m^3), $c_{f,i}$ is the species concentration (SI unit: mol/m^3) of the associated feed stream $v_{f,i}$ (SI unit: m^3/s), and R_i denotes the species rate expression (SI unit: mol/(m^3·s)). V_r labels the reactor volume (SI unit: m^3) and is a function of time. For ideal mixtures:

$$\frac{dV_r}{dt} = \sum v_{f,i} + v_p$$

where v_p is the volumetric production rate due to chemical reaction:

$$v_p = \sum_j \sum_i \nu_{ij} \frac{M_i}{\rho_i} r_j V_r \tag{2}$$

In Equation 2, ν_{ij} is the stoichiometric coefficient of species i in reaction j, M_i denotes the species molecular weight (SI unit: kg/mol), ρ_i is the species density (SI unit: kg/m^3), and r_j is the reaction rate (SI unit: mol/(m^3·s)) of reaction j.

In the present example, the density of the monomer is 800 kg/m^3, 1100 kg/m^3 for the polymer, and 1000 kg/m^3 for water. Hence, as polymer is being formed, the volume of

the reacting mixture decreases (v_p is negative). The model investigates two operating conditions:

- *Operating condition 1* — The monomer feed (1 m^3/min) is shut off once the reactor volume reaches 20 m^3, which occurs after 11.2 minutes. The reaction is then allowed to go to completion.
- *Operating condition 2* — The monomer feed is adjusted to keep the reactor filled while the reaction goes to completion. This is accomplished by setting the volumetric feed equal to $-v_p$, for t > 11.2 minutes.

Results

Figure 2 illustrates the volumetric flow rate of the feed stream, v_f.

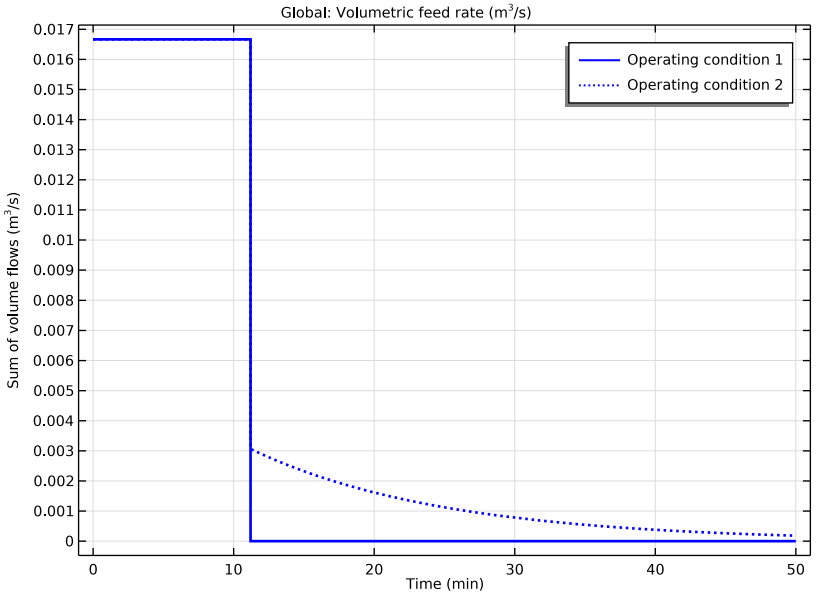

Figure 2: The volumetric flow rate of the feed stream (m^3/s) as function of time (minutes) for operating condition 1 (solid line) and 2 (dash-dotted line).

Figure 3 shows the reactor volume as function of the runtime, illustrating the two operating conditions listed above.

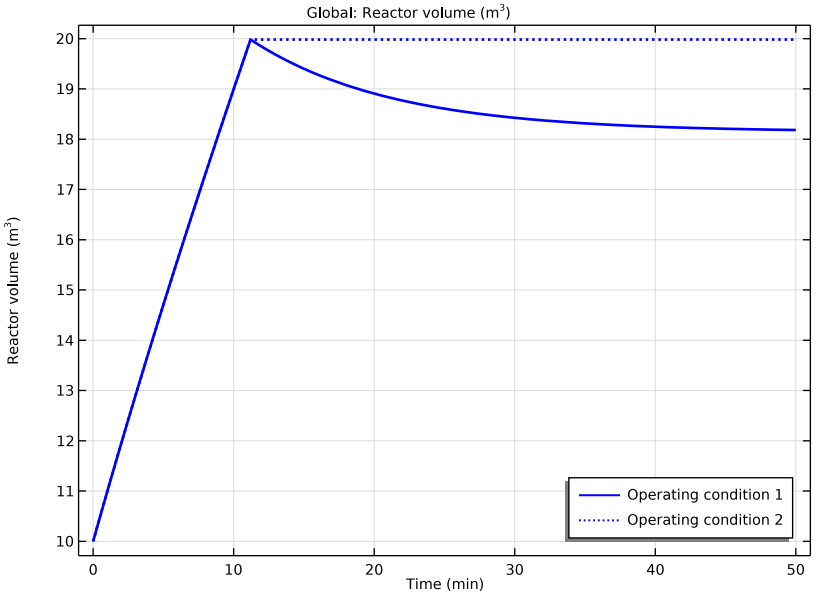

Figure 3: The reactor volume (m^3) as function of time (minutes) for operating condition 1 (solid line) and 2 (dash-dotted line).

Figure 4 shows the total mass of monomer in the reactor, m_M (kg), as evaluated by the expression:

$$m_M = c_M V_r M_M$$

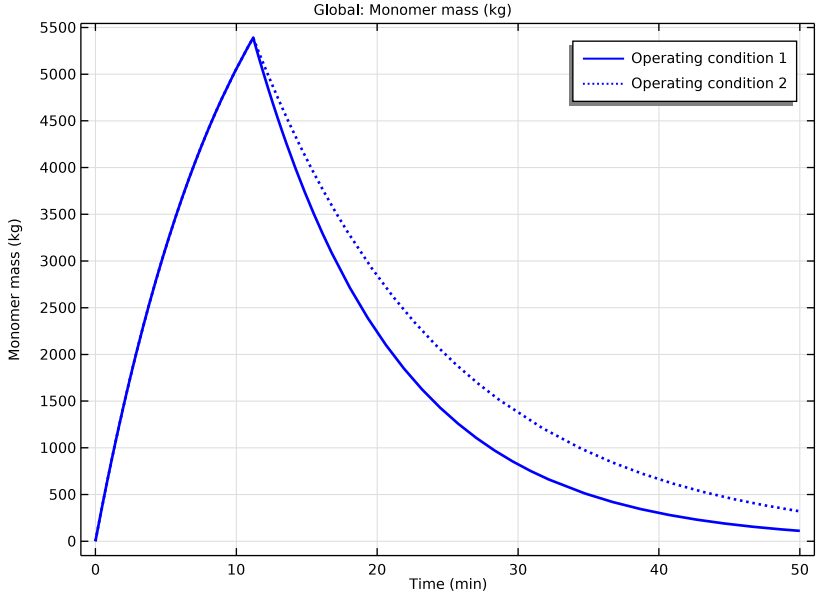

Figure 4: The total monomer mass in the reactor volume (kg) as function of time (minutes) for operating condition 1 (solid line) and 2 (dash-dotted line).

It is straightforward to compare the amount of produced polymer as a result of the different operating conditions. For both cases the reaction has run to completion after approximately 50 minutes. At this time, the total volume of the reacting mixture is 18.2 m^3 for operating condition 1 and 20 m^3 for operating condition 2.

The relative increase in polymer production using operating condition 2 compared to condition 1 is then:

$$\frac{m_{P,2} - m_{P,1}}{m_{P,1}} = \frac{c_{P,2} V_{r,2} M_P - c_{P,1} V_{r,1} M_P}{c_{P,1} V_{r,1} M_P} = \frac{10.5 - 8.8}{8.8} = 19.3\%$$

Reference

1. J.B. Rawlings and J.G. Ekerdt, *Chemical Reactor Analysis and Design Fundamentals*, Nob Hill Publishing, example 4.3, pp. 139–144, 2004.

Application Library path: `Chemical_Reaction_Engineering_Module/Ideal_Tank_Reactors/semibatch_polymerization`

Modeling Instructions

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 text file provided with the **Model 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 `semibatch_polymerization_parameters.txt`.

Step 1 (step1)

Add a step function that regulates the volumetric feed rate during the operations.

1 In the **Home** toolbar, click **Functions** and choose **Global>Step**.

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

3 In the **Location** text field, type `t_cond`.

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 **Semibatch**.

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

Reaction 1

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

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

3 In the **Formula** text field, type `M=>P`.

4 Locate the **Rate Constants** section. In the k^{f} text field, type `kf_reaction`.

Species: M

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

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

3 In the M text field, type `Mm_M`.

4 In the ρ text field, type `density_M`.

Species: P

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

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

3 In the M text field, type `Mm_P`.

4 In the ρ text field, type `density_P`.

The reaction takes place in water.

Species 1

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

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

3 In the text field, type `H2O`.

4 Locate the **General Parameters** section. In the M text field, type `Mm_H2O`.

5 In the ρ text field, type `density_H2O`.

DEFINITIONS

Add the two filling conditions as variables dependent on the step function and the monomer mass expression. This is retrieved from a data text file provided with the **Model Library**.

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 `semibatch_polymerization_variables.txt`.

REACTION ENGINEERING (RE)

Feed Inlet 1

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

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

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

4 Locate the **Feed Inlet Concentration** section. In the **Feed inlet concentration** table, enter the following settings:

Species	Concentration (mol/m^3)
H2O	`cinlet_H2O`
M	`cinlet_M`

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 V_{r0} text field, type `Vr_init`.

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

Species	Concentration (mol/m^3)
H2O	`cinit_H2O`

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 In the **Output times** text field, type `range(0,0.1,3000)`.

4 In the **Home** toolbar, click **Compute**.

RESULTS

Global 1

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

2 In the **Settings** window for **Global**, locate the **x-Axis Data** section.

3 From the **Parameter** list, choose **Expression**.

4 In the **Expression** text field, type `t`.

5 From the **Unit** list, choose **min**.

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

STUDY 1

Use the **Parametric Sweep** feature to investigate the difference when the compensating fill is turned on.

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
fill (Control parameter for filling)	0 1	

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

RESULTS

Volumetric feed rate

In the **Settings** window for **1D Plot Group**, type `Volumetric feed rate` in the **Label** text field.

Global 1

1 In the **Model Builder** window, expand the **Volumetric feed rate** 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.sumvf - Sum of volume flows - m³/s**.

3 Click to expand the **Title** section. From the **Title type** list, choose **Manual**.

4 In the **Title** text area, type `Global: Volumetric feed rate (m<sup>3</sup>/s)`.

5 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

6 In the **Expression** text field, type `t`.

7 From the **Unit** list, choose **min**.

8 Click to expand the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Cycle**.

9 From the **Color** list, choose **Blue**.

10 In the **Width** text field, type `2`.

11 Click to expand the **Legends** section. From the **Legends** list, choose **Manual**.

12 In the table, enter the following settings:

Legends
Operating condition 1
Operating condition 2

13 In the **Volumetric feed rate** toolbar, click **Plot**.

Reactor volume

1 In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Reactor volume` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.

4 Locate the **Legend** section. From the **Position** list, choose **Lower right**.

Global 1

1 Right-click **Reactor volume** and choose **Global**.

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.Vr - Reactor volume - m³**.

3 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

4 In the **Expression** text field, type `t`.

5 From the **Unit** list, choose **min**.

6 Locate the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Cycle**.

7 From the **Color** list, choose **Blue**.

8 In the **Width** text field, type `2`.

9 Locate the **Legends** section. From the **Legends** list, choose **Manual**.

10 In the table, enter the following settings:

Legends
Operating condition 1
Operating condition 2

11 In the **Reactor volume** toolbar, click **Plot**.

Monomer mass

1 In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Monomer mass` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.

Global 1

1 Right-click **Monomer mass** and choose **Global**.

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)>Definitions> Variables>m_mon - Monomer mass - kg**.

3 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

4 In the **Expression** text field, type `t`.

5 From the **Unit** list, choose **min**.

6 Locate the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **Cycle**.

7 From the **Color** list, choose **Blue**.

8 In the **Width** text field, type `2`.

9 Locate the **Legends** section. From the **Legends** list, choose **Manual**.

10 In the table, enter the following settings:

Legends
Operating condition 1
Operating condition 2

11 In the **Monomer mass** toolbar, click **Plot**.