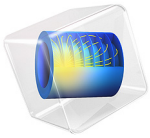


Crystallization of Benzoic Acid in a Mixed Suspension, Mixed Product Removal Crystallizer

Introduction

Crystallization is a key separation process in chemical engineering. Hundreds of millions of tons of materials are produced by crystallization yearly. Some examples of materials produced by crystallization include sodium chloride, sodium sulphates and sucrose. A main motivation for using crystallization is that separating a product from a solution by crystallizing it out of solution usually requires less energy than evaporating the solvent.

Crystallization takes place in two steps. First, a crystal nuclei must form (nucleation). Second, the nuclei grows by deposition of more crystal material (growth). The driving force for crystallization is the degree of supersaturation. Supersaturation can be achieved for example by cooling the solution. Upon cooling, the solution becomes supersaturated, and crystallization can begin. The key objective in designing and operating a crystallizer is to control the crystal size distribution. For example, in the crystallization of a pharmaceutical product, the size of the crystals formed will determine the time the product will take to dissolve in the stomach of a patient.

In this example, the crystallization of benzoic acid is modeled in an idealized continuous crystallizer known as a "mixed suspension, mixed product removal reactor". A 0D model is defined, and a population balance equation is solved to calculate the crystal size distribution and the mean particle size under different conditions. The model is based on a paper by Morris and others (Ref. 1). Figure 1 shows a sketch of the crystallizer setup.

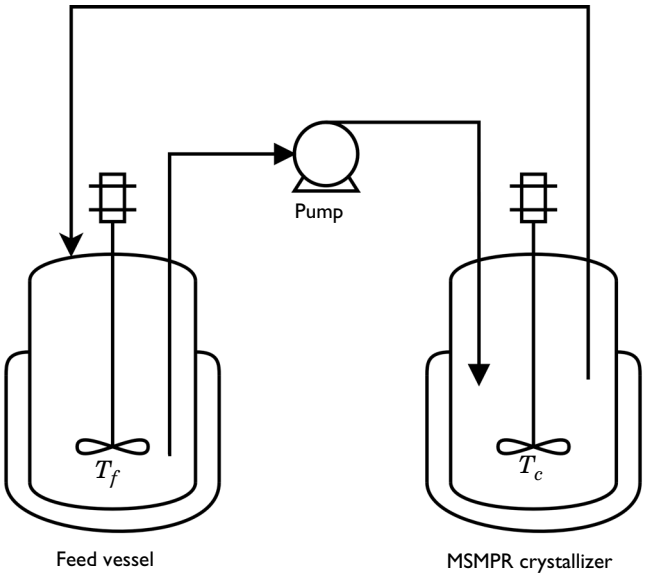


Figure 1: Sketch of the MSMPR setup. The crystallizer is kept at a temperature below that of the feed to create supersaturation.

Model Definition

The crystallization of benzoic acid is modeled in 0D. The crystallizer and the feed vessel are both assumed to be perfectly mixed and operated in steady state. Kinetic parameters fitted to experimental data in Ref. 1 are used.

For an ideal MSMPR crystallizer, the analytical solution to the population balance equation is

$$n = n^0 \exp\left(-\frac{L}{G\tau}\right), \tag{1}$$

where n is the population density, n^0 is the nuclei population density, L is the crystal size, G is the crystal growth rate, and τ is the mean residence time. The mass-based mean crystal size distribution is found by taking the ratio of the fourth and third moments of n as defined by Equation 1. The nuclei population density is obtained from

$$n^0 = \frac{B^0}{G}, \tag{2}$$

where B^0 is the nucleation rate. The nucleation rate is given by

$$B^0 = k_b M_T^j \Delta C^b, \tag{3}$$

where k_b is a nucleation rate coefficient, M_T is the MSMPR suspension crystal weight fraction, ΔC is the driving force for crystallization, and j and b are dimensionless parameters. The driving force for crystallization is given by

$$\Delta C = C - C^*(T), \tag{4}$$

where C is the benzoic acid mass fraction (g benzoic acid/kg solvent) in the MSMPR crystallizer, and $C^*(T)$ is the saturation mass fraction.

The saturation mass fraction is obtained from a polynomial expression determined experimentally for a mixture of benzoic acid in 1.5:1 (w/w) water/ethanol:

$$C^*(T) = 2.03 \times 10^{-5} T^4 + 2.97 \times 10^{-4} T^3 + 4.70 \times 10^{-2} T^2 + 1.43T + 24.71 \tag{5}$$

A graphical representation of C^* is found in Figure 2.

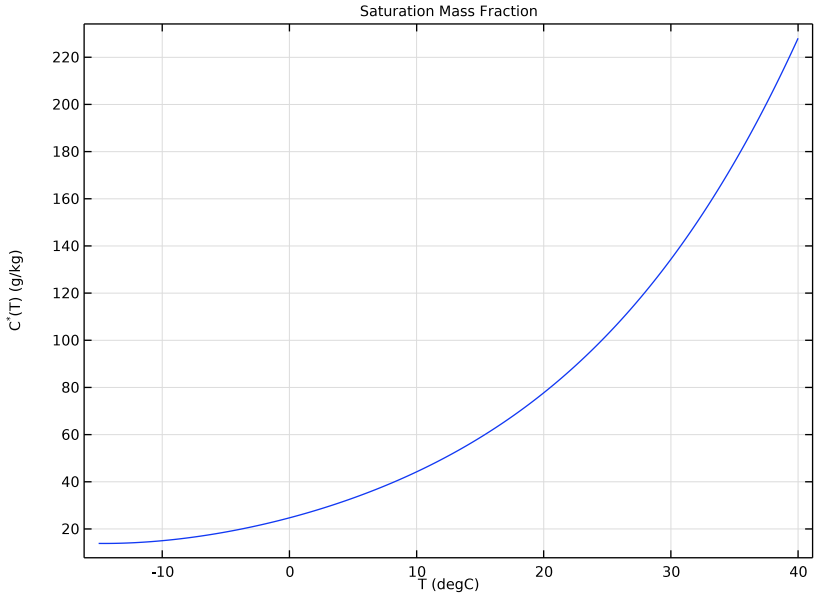


Figure 2: The saturation mass fraction of benzoic acid as a function of temperature.

The growth rate is obtained from

$$G = k_g \Delta C^g, \tag{6}$$

where k_g is the crystal growth rate coefficient and g is a fitted kinetic parameter. In turn, the crystal growth rate coefficient is obtained from

$$k_g = k_{g0} \exp\left(-\frac{E_g}{RT}\right), \tag{7}$$

where k_{g0} is the Arrhenius expression pre-exponential factor, and E_g is the activation energy for crystal growth.

Solving for the crystal concentration allows the population density to be determined. A mass balance on the crystallizer gives the equation

$$C_0 - C = M_T. \tag{8}$$

Here, C_0 is the concentration of benzoic acid in the feed. Furthermore, the suspension crystal weight fraction is related to the nuclei population density and the growth rate through

$$M_T = 6k_v\rho_c n^0 (G\tau)^4, \tag{9}$$

where k_v and ρ_c are the volumetric shape factor and density of the crystals, respectively.

The crystal concentration is obtained by solving for the difference of these two definitions of M_T, that is

$$M_{T,(8)} - M_{T,(9)} = 0. \tag{10}$$

Equation 10 is solved for in a **Global Equations** node.

The steady-state mass-weighted mean crystal size, $L_{4,3}$, is calculated from the ratio of the fourth and third moments of the crystal size distribution, using the following expression:

$$L_{4,3} = \frac{\int_0^\infty nL^4 dL}{\int_0^\infty nL^3 dL} \tag{11}$$

Results and Discussion

Crystal size distributions are determined for the experimental setup giving the largest and smallest crystal sizes, and for sweeps from low to high reactor temperature, and low to high residence time. Finally, the effect on the mean particle size of both reactor temperature, and of residence time, is examined.

CRYSTAL SIZE DISTRIBUTIONS

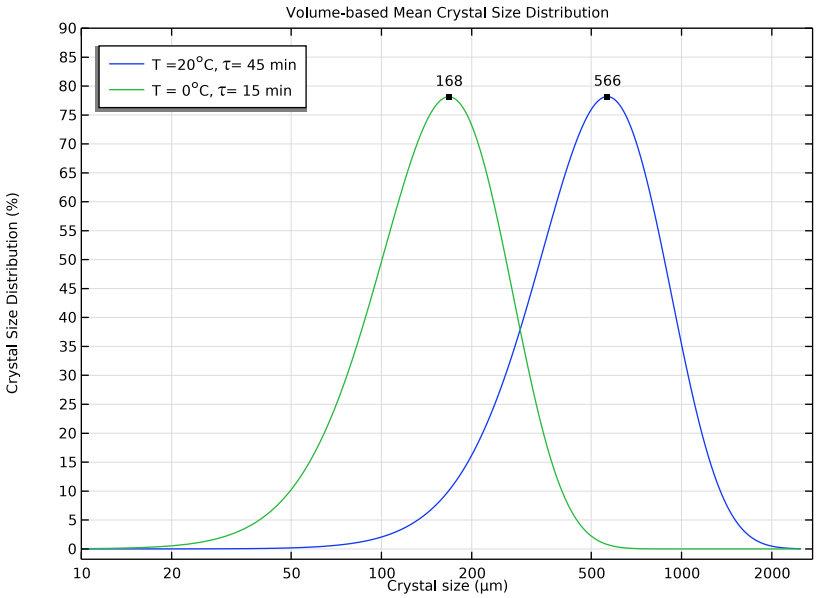


Figure 3: Crystal size distributions for the experimental conditions where the smallest and largest particles are produced.

Figure 3 shows the crystal size distributions for the combinations of temperature and residence time that results in production of the smallest and the largest particles. These results agree well with those from Ref. 1.

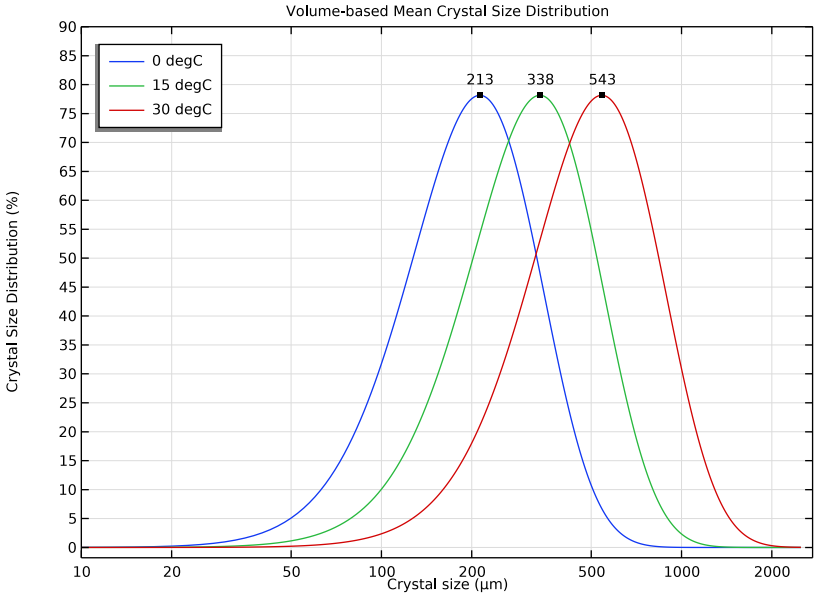


Figure 4: Crystal size distributions for increasing crystallizer temperatures.

Figure 2 shows that the saturation mass fraction of benzoic acid increases with temperature. This reduces the driving force for crystallization, ΔC. At the same time, the growth rate of the crystals increases with increasing temperature, according to Equation 6. The effect on the crystal size distribution is that the crystals that do form, grow to larger average sizes. Increasing the residence time also has a similar effect, as seen in Figure 5.

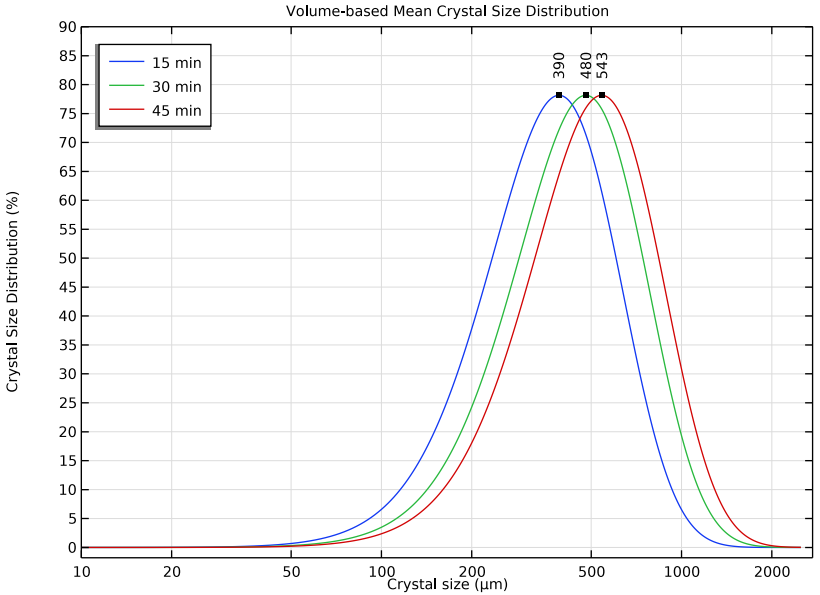


Figure 5: The effect of residence time on the crystal size distribution.

MEAN PARTICLE SIZE

Figure 6 and Figure 7 show the average crystal size for different temperatures and residence times, respectively.

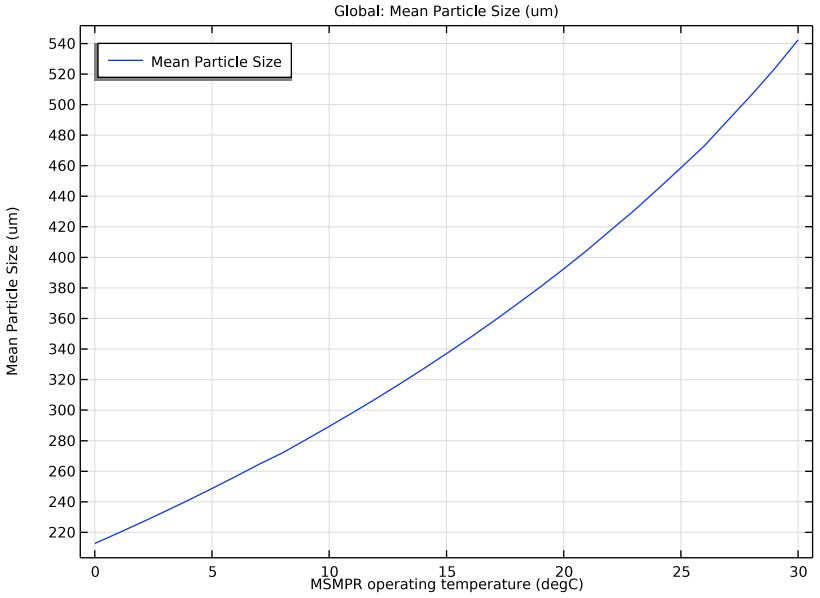


Figure 6: The effect of temperature on the average particle size. The residence time is 45 min.

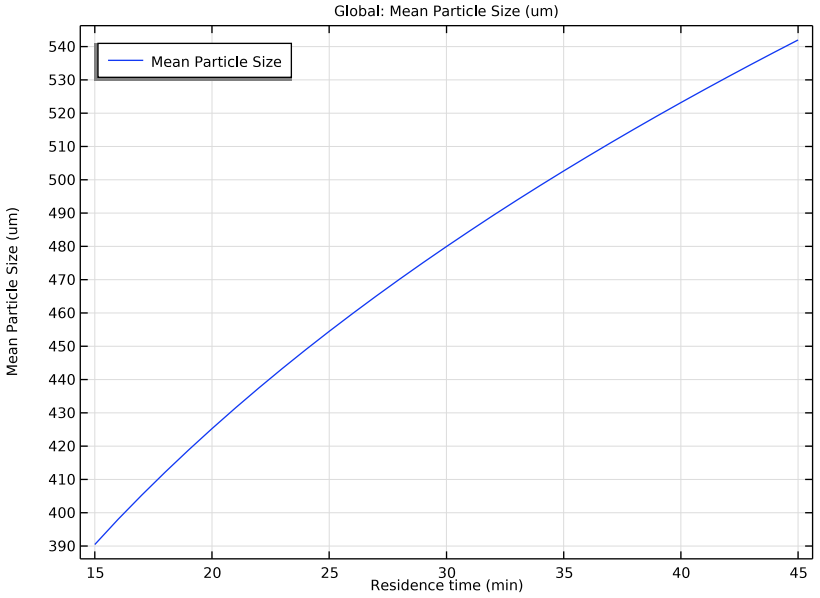


Figure 7: The effect of residence time on the average particle size. The crystallizer temperature is 30°C.

Notes About the COMSOL Implementation

The original paper (Ref. 1) defined crystal concentrations in both g/ml solvent and g/g solvent, but for simplicity, this model defines concentrations only in g/kg solvent. This does not affect the resulting crystal size distributions.

References

1. G. Morris, G. Power, S. Ferguson, M. Barrett, G.Hou, and B. Glennon, "Estimation of Nucleation and Growth Kinetics of Benzoic Acid by Population Balance Modeling of a Continuous Cooling Mixed Suspension, Mixed Product Removal Crystallizer," *Org. Process Res. Dev.*, vol. 19, pp. 1891–1902, 2015.

2. J.F. Richardson, J.H. Harker, and J.R. Backhurst, *Coulson & Richardson's Chemical Engineering*, vol. 2, 5th edition, Elsevier, 2002.

Application Library path: `Chemical_Reaction_Engineering_Module/Mixing_and_Separation/benzoic_acid_crystallization`

Modeling Instructions

A 0D model using a Global Equations interface will be used to describe the crystallization process.

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 **Mathematics>ODE and DAE Interfaces> Global ODEs and DAEs (ge)**.

3 Click **Add**.

4 Click **Study**.

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

6 Click **Done**.

Import the parameters for the model.

GLOBAL DEFINITIONS

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 `benzoic_acid_crystallization_parameters.txt`.

5 In the **Home** toolbar, click **Parameter Case**.

Define two parameter cases to simulate the conditions that give rise to the smallest and the largest crystals.

6 In the **Settings** window for **Case**, type `Experiment Giving Largest Crystals` in the **Label** text field.

7 In the **Home** toolbar, click **Parameter Case**.

8 In the **Settings** window for **Case**, type `Experiment Giving Smallest Crystals` in the **Label** text field.

9 Locate the **Parameters** section. In the table, enter the following settings:

Name	Expression	Description
T	`0[degC]`	MSMPR operating temperature
tau	`20 [min]`	Residence time

Define a Function representing the saturation mass fraction.

Saturation Mass Fraction

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

2 In the **Settings** window for **Analytic**, type `Saturation Mass Fraction` in the **Label** text field.

3 In the **Function name** text field, type `C_star`.

4 Locate the **Definition** section. In the **Expression** text field, type `2.03e-5*T^4 + 2.97e-4*T^3 + 4.70e-2*T^2 + 1.43*T + 24.71`.

5 In the **Arguments** text field, type `T`.

6 Locate the **Units** section. In the **Function** text field, type `g/kg`.

7 In the table, enter the following settings:

Argument	Unit
T	`degC`

8 Locate the **Plot Parameters** section. In the table, enter the following settings:

Plot	Argument	Lower limit	Upper limit	Fixed value	Unit
√	T	`-15[degC]`	`40[degC]`	0	K

9 Click **Create Plot**.

RESULTS

Saturation Mass Fraction

1 In the **Settings** window for **1D Plot Group**, type `Saturation Mass Fraction` in the **Label** text field.

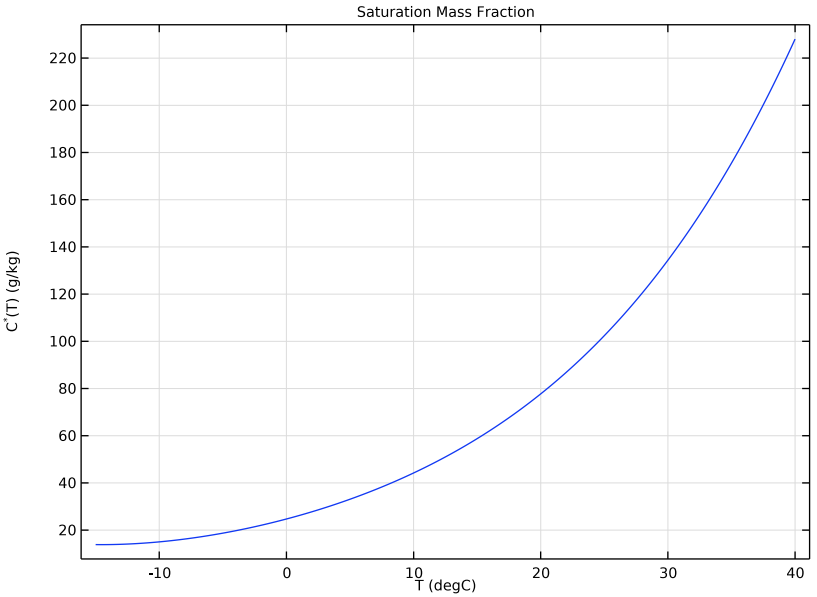
2 Click to expand the **Title** section. In the **Title** text area, type `Saturation Mass Fraction`.

3 Locate the **Plot Settings** section.

4 Select the **y-axis label** check box. In the associated text field, type `C<sup>*</sup>(T) (g/kg)`.

5 In the **Saturation Mass Fraction** toolbar, click **Plot**.

The saturation mass fraction increases with temperature. Decreasing the temperature is a key driving force for crystallization.



To simplify the model setup, import the required variable expressions from a separate file.

DEFINITIONS

Variables 1

1 In the **Home** toolbar, click **Variables** and choose **Local 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 `benzoic_acid_crystallization_variables.txt`.

Define the global equation that will be solved to obtain the benzoic acid mass fraction.

GLOBAL ODES AND DAES (GE)

Global Equations 1 (ODE1)

1 In the **Model Builder** window, under **Component 1 (comp1)>Global ODEs and DAEs (ge)** click **Global Equations 1 (ODE1)**.

2 In the **Settings** window for **Global Equations**, locate the **Global Equations** section.

3 In the table, enter the following settings:

Name	f(u,ut,utt, t) (1)	Initial value (u_0) (1)	Initial value (u_t0) (1/s)	Description
C	M_T_MB-M_T_MR	C_star(T)+1[g/kg]	0	Benzoic acid mass fraction

4 Locate the **Units** section. Click **Define Dependent Variable Unit**.

5 In the **Dependent variable quantity** table, enter the following settings:

Dependent variable quantity	Unit
Custom unit	g/kg

6 Click **Define Source Term Unit**.

7 In the **Source term quantity** table, enter the following settings:

Source term quantity	Unit
Custom unit	g/kg

STUDY 1: EXTREME CASES

1 In the **Model Builder** window, click **Study 1**.

2 In the **Settings** window for **Study**, type `Study 1: Extreme Cases` in the **Label** text field.

Parametric Sweep

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

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

3 From the **Sweep type** list, choose **Parameter switch**.

4 Click **Add**.

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

Plot the crystal size distributions for the experiments giving the smallest and the largest crystals .

RESULTS

Grid 1D: Extreme Cases

1 In the **Results** toolbar, click **More Datasets** and choose **Grid>Grid 1D**.

2 In the **Settings** window for **Grid 1D**, type `Grid 1D: Extreme Cases` in the **Label** text field.

3 Locate the **Parameter Bounds** section. In the **Name** text field, type `L`.

4 Locate the **Data** section. From the **Dataset** list, choose **Study 1: Extreme Cases/ Parametric Solutions 1 (sol2)**.

5 Locate the **Parameter Bounds** section. In the **Maximum** text field, type `L_max`.

CSD for Extreme Cases

1 In the **Results** toolbar, click **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `CSD for Extreme Cases` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Grid 1D: Extreme Cases**.

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

5 In the **Title** text area, type `Volume-based Mean Crystal Size Distribution`.

6 Locate the **Plot Settings** section.

7 Select the **y-axis label** check box. In the associated text field, type `Crystal Size Distribution (%)`.

8 Locate the **Axis** section. Select the **x-axis log scale** check box.

9 Locate the **Legend** section. From the **Position** list, choose **Upper left**.

Line Graph 1

1 In the **CSD for Extreme Cases** toolbar, click **Line Graph**.

2 In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `(n0 * exp(- L / (G*tau))*L^4)/ integrate((n0 * exp(- L / (G*tau)))*L^3, L, 0, L_max)`.

4 From the **Unit** list, choose **%**.

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

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

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

8 Select the **Description** check box. In the associated text field, type `Crystal size`.

9 Click to expand the **Legends** section. Select the **Show legends** check box.

10 From the **Legends** list, choose **Manual**.

11 In the table, enter the following settings:

Legends
`T =20\deg C, \tau = 45 min`
`T = 0\deg C, \tau = 15 min`

12 In the **CSD for Extreme Cases** toolbar, click **Plot**.

Graph Marker 1

1 In the **Model Builder** window, right-click **Line Graph 1** and choose **Graph Marker**.

2 In the **Settings** window for **Graph Marker**, locate the **Text Format** section.

3 In the **Display precision** text field, type 3.

4 Select the **Show x-coordinate** check box.

5 Clear the **Show y-coordinate** check box.

6 Click to expand the **Coloring and Style** section. From the **Anchor point** list, choose **Lower middle**.

7 In the **CSD for Extreme Cases** toolbar, click **Plot**.

CSD for Extreme Cases

1 In the **Model Builder** window, under **Results** click **CSD for Extreme Cases**.

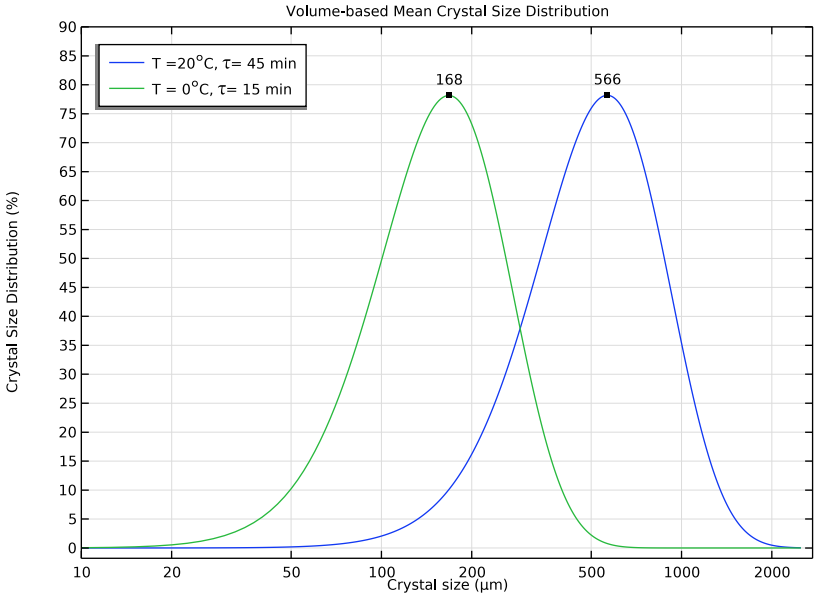
2 In the **Settings** window for **1D Plot Group**, locate the **Axis** section.

3 Select the **Manual axis limits** check box.

4 In the **x minimum** text field, type 10.

5 In the **y maximum** text field, type 90.

6 In the **CSD for Extreme Cases** toolbar, click **Plot**.



Next, we'll set up a study to calculate the effect of temperature on the crystal size. For this study, the longest residence time will be used.

ADD STUDY

1 In the **Home** toolbar, click **Add Study** to open the **Add Study** window.

2 Go to the **Add Study** window.

3 Find the **Studies** subsection. In the **Select Study** tree, select **General Studies>Stationary**.

4 Click **Add Study** in the window toolbar.

5 In the **Home** toolbar, click **Add Study** to close the **Add Study** window.

STUDY 2: TEMPERATURE SWEEP

1 In the **Model Builder** window, click **Study 2**.

2 In the **Settings** window for **Study**, type `Study 2: Temperature Sweep` in the **Label** text field.

Step 1: Stationary

1 In the **Model Builder** window, under **Study 2: Temperature Sweep** click **Step 1: Stationary**.

2 In the **Settings** window for **Stationary**, click to expand the **Study Extensions** section.

3 Select the **Auxiliary sweep** check box.

4 Click + **Add**.

5 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
T (MSMPR operating temperature)	`range(0,1,30)`	`degC`

Solution 5 (sol5)

1 In the **Study** toolbar, click **Show Default Solver**.

2 In the **Model Builder** window, expand the **Solution 5 (sol5)** node, then click **Stationary Solver 1**.

3 In the **Settings** window for **Stationary Solver**, locate the **General** section.

4 In the **Relative tolerance** text field, type `0.0001`.

Reduce the solver tolerance to avoid numerical noise in the temperature sweep results.

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

RESULTS

Grid 1D: Extreme Cases

In the **Model Builder** window, under **Results>Datasets** right-click **Grid 1D: Extreme Cases** and choose **Duplicate**.

Grid 1D: Temperature Sweep

1 In the **Model Builder** window, under **Results>Datasets** click **Grid 1D: Extreme Cases 1**.

2 In the **Settings** window for **Grid 1D**, type `Grid 1D: Temperature Sweep` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 2: Temperature Sweep/ Solution 5 (sol5)**.

CSD for Extreme Cases

In the **Model Builder** window, under **Results** right-click **CSD for Extreme Cases** and choose **Duplicate**.

CSD for Temperature Sweep

1 In the **Model Builder** window, under **Results** click **CSD for Extreme Cases 1**.

2 In the **Settings** window for **1D Plot Group**, type `CSD for Temperature Sweep` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Grid 1D: Temperature Sweep**.

4 From the **Parameter selection (T)** list, choose **From list**.

5 In the **Parameter values (T (degC))** list, choose **0**, **15**, and **30**.

Line Graph 1

1 In the **Model Builder** window, expand the **CSD for Temperature Sweep** node, then click **Line Graph 1**.

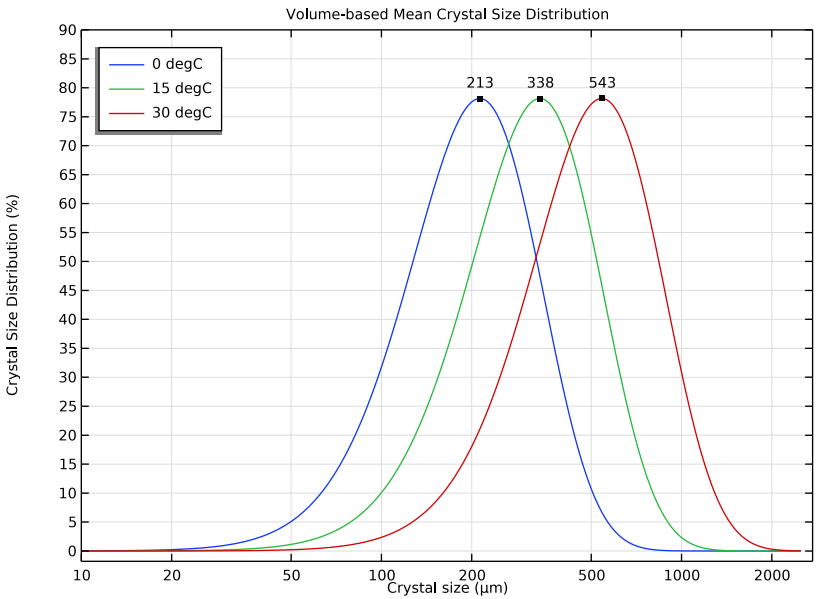
2 In the **Settings** window for **Line Graph**, locate the **Legends** section.

3 From the **Legends** list, choose **Automatic**.

CSD for Temperature Sweep

1 In the **Model Builder** window, click **CSD for Temperature Sweep**.

2 In the **CSD for Temperature Sweep** toolbar, click **Plot**.



Next, we'll set up a study to calculate the effect of residence time on the crystal size. For this study, the highest temperature will be used.

ADD STUDY

1 In the **Home** toolbar, click **Add Study** to open the **Add Study** window.

2 Go to the **Add Study** window.

3 Find the **Studies** subsection. In the **Select Study** tree, select **General Studies>Stationary**.

4 Click **Add Study** in the window toolbar.

5 In the **Home** toolbar, click **Add Study** to close the **Add Study** window.

STUDY 3: RESIDENCE TIME SWEEP

1 In the **Model Builder** window, click **Study 3**.

2 In the **Settings** window for **Study**, type `Study 3: Residence Time Sweep` in the **Label** text field.

Step 1: Stationary

1 In the **Model Builder** window, under **Study 3: Residence Time Sweep** click **Step 1: Stationary**.

2 In the **Settings** window for **Stationary**, locate the **Study Extensions** section.

3 Select the **Auxiliary sweep** check box.

4 Click **Add**.

5 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
tau (Residence time)	`range(15,1,45)`	`min`

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

RESULTS

Grid 1D: Temperature Sweep

In the **Model Builder** window, under **Results>Datasets** right-click **Grid 1D: Temperature Sweep** and choose **Duplicate**.

Grid 1D: Residence Time Sweep

1 In the **Model Builder** window, under **Results>Datasets** click **Grid 1D: Temperature Sweep 1**.

2 In the **Settings** window for **Grid 1D**, type `Grid 1D: Residence Time Sweep` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 3: Residence Time Sweep/ Solution 6 (sol6)**.

CSD for Temperature Sweep

In the **Model Builder** window, under **Results** right-click **CSD for Temperature Sweep** and choose **Duplicate**.

CSD for Residence Time Sweep

1 In the **Model Builder** window, under **Results** click **CSD for Temperature Sweep 1**.

2 In the **Settings** window for **1D Plot Group**, type `CSD for Residence Time Sweep` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Grid 1D: Residence Time Sweep**.

4 In the **Model Builder** window, expand the **CSD for Residence Time Sweep** node.

Graph Marker 1

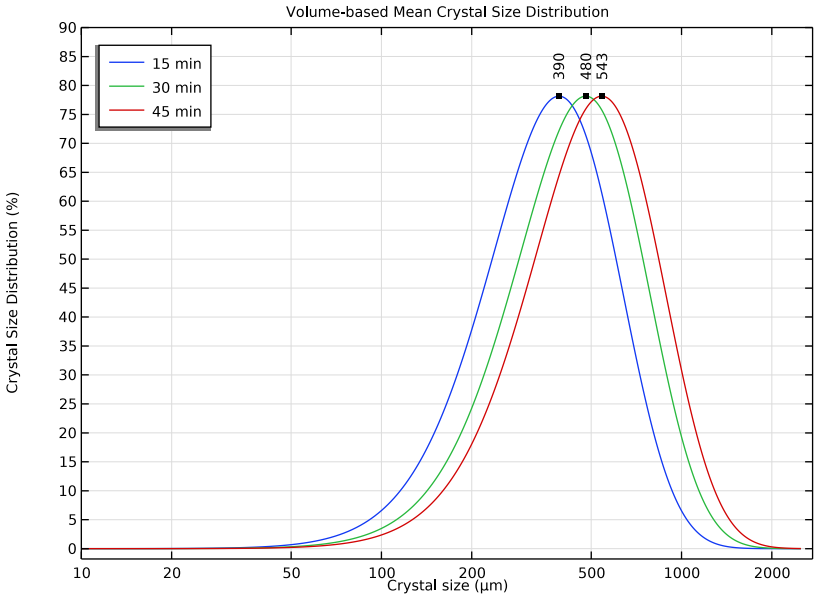
1 In the **Model Builder** window, expand the **Results>CSD for Residence Time Sweep> Line Graph 1** node, then click **Graph Marker 1**.

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

3 From the **Orientation** list, choose **Vertical**.

4 From the **Anchor point** list, choose **Middle left**.

5 In the **CSD for Residence Time Sweep** toolbar, click **Plot**.



Mean Particle Size for Different Operating Temperatures

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

Finally, create two plots showing the effect on average particle size of temperature, and residence time, respectively.

2 In the **Settings** window for **1D Plot Group**, type `Mean Particle Size for Different Operating Temperatures` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 2: Temperature Sweep/ Solution 5 (sol5)**.

4 Locate the **Legend** section. From the **Position** list, choose **Upper left**.

Global 1

1 In the **Mean Particle Size for Different Operating Temperatures** toolbar, click  **Global**.

The mean particle size plots do not use a Grid dataset. For this reason, L is not defined. We will instead use the formal integration constant parameter L_int.

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

3 In the table, enter the following settings:

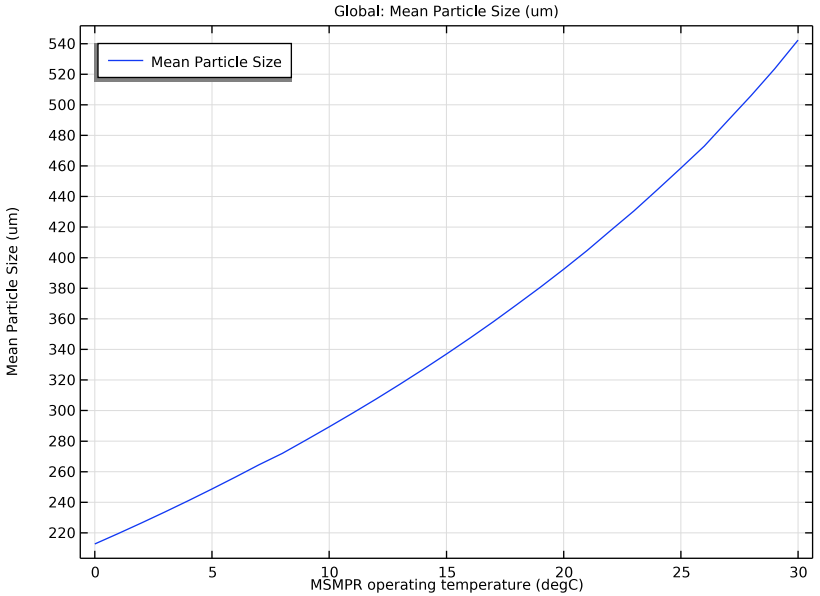
Expression	Unit	Description
`integrate(n0 * exp(- L_int / (G*tau))* L_int^4, L_int, 0, L_max) / integrate((n0 * exp(- L_int / (G* tau)))*L_int^3, L_int, 0, L_max)`	`um`	`Mean Particle Size`

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

5 In the **Expression** text field, type `T`.

6 From the **Unit** list, choose **degC**.

7 In the **Mean Particle Size for Different Operating Temperatures** toolbar, click **Plot**.



Mean Particle Size for Different Operating Temperatures

In the **Model Builder** window, right-click **Mean Particle Size for Different Operating Temperatures** and choose **Duplicate**.

Mean Particle Size for Different Residence Times

1 In the **Model Builder** window, under **Results** click **Mean Particle Size for Different Operating Temperatures 1**.

2 In the **Settings** window for **1D Plot Group**, type `Mean Particle Size for Different Residence Times` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 3: Residence Time Sweep/ Solution 6 (sol6)**.

Global 1

1 In the **Model Builder** window, expand the **Mean Particle Size for Different Residence Times** node, then click **Global 1**.

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

3 In the **Expression** text field, type `tau`.

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

5 In the **Mean Particle Size for Different Residence Times** toolbar, click **Plot**.