# Week 9- Exercise

Problem:

The cumulative particle size distribution $N(L)$ has been measured for two different MSMPR crystallization processes (A and B) and is reported in the figure below. Both processes are producing the same compact crystals, under different residence times and temperatures. The growth rate is known to be independent from both temperature and composition ($G = const$). The nucleation rate J instead depends exponentially on the inverse of the temperature through an Arrhenius-like expression ($J = A\exp(-B/T)$, where A and B are constants).
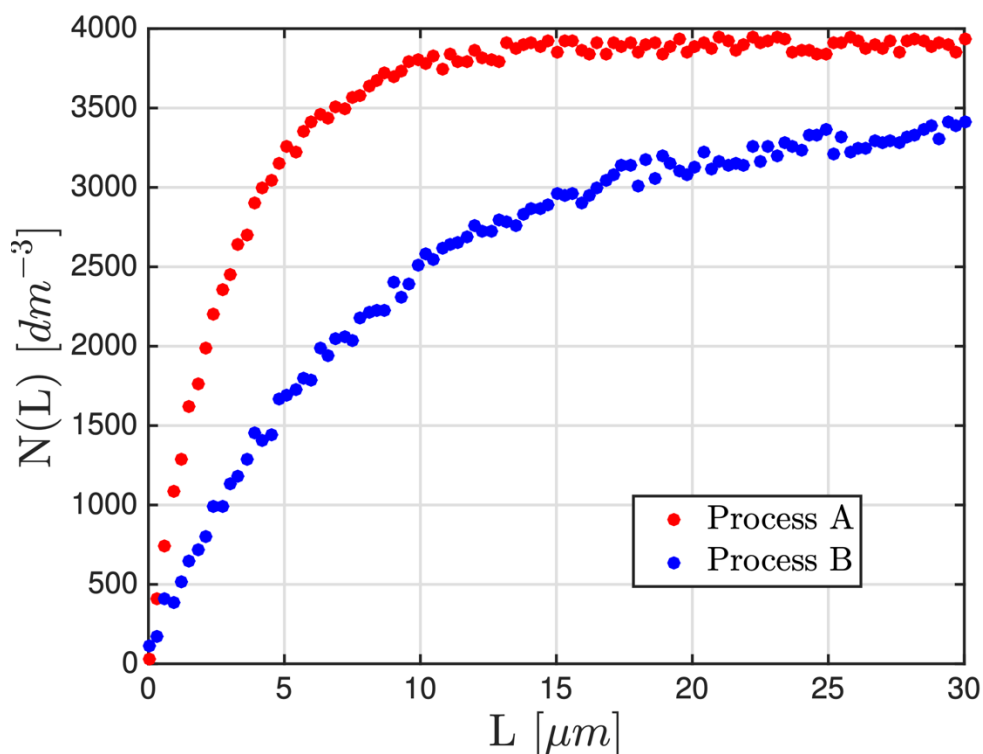
Tasks:

(a) Compute and plot the number density, length, area, and normalized mass distribution for these two processes. Use the dataset provided.

(b) Compute the dominant length L_D obtained from both processes.

(c) Can you say anything about the residence time in the two crystallizers?

(d) Which process is operating at the highest temperature?

(a) Compute and plot the number density, length, area, and normalized mass distribution for these two processes. Use the dataset provided.

First, we need to fit the data to an equation, from the steady state number population density:

$$\frac{dN(L)}{dL} = n(L) = n_0 \cdot \exp\left(-\frac{L}{G\tau}\right)$$

$$\rightarrow N(L) = -n_0 \cdot G\tau \cdot \exp\left(-\frac{L}{G\tau}\right) + k$$

Because we assume that the growth rate, G, is independent from the crystal size, L, $\rightarrow G\tau = const.$

Let $Y = G\tau$,

$$\rightarrow N(L) = -n_0 \cdot Y \cdot \exp\left(-\frac{L}{Y}\right) + k$$

We will fit the data to the equation above, but first we need to find n_0. By definition,

$$\frac{dN}{d(L = 0)} = n_0$$

Therefore, from the data given we can approximate n_0 as the derivative close to $L = 0$,

For Process A:
$$n_{0,A} = \frac{413.25 - 32.366}{0.3 - 0} = 1269.6133 \ \mu m^{-1} dm^{-3}$$

For Process B:
$$n_{0,B} = \frac{404.64 - 114.95}{0.6 - 0} = 482.8167 \ \mu m^{-1} dm^{-3}$$

Now, by trial and error, we an estimate parameters $Y_{A,B}$ and $k_{A,B}$, by using 2 values from the data sets, and solving two equations simultaneously, and see how the parameters fits with the data. We will use the parameters that, when plotted, give the line of best fit.

For process A:
Take the initial value, $N_A(L = 0) = 32.366 \ dm^{-3}$
Take a value from the end of the data set, $N_A(L = 14.4) = 3889.9 \ dm^{-3}$

Formulate the two equations,

$$-(1269.6133) \cdot Y_A + k_A = 32.366 \qquad\qquad \text{(Eq. 1)}$$

$$-(1269.6133) \cdot Y_A \cdot \exp\left(-\frac{14.4}{Y}\right) + k_A = 3889.9 \qquad\qquad \text{(Eq. 2)}$$

Solving in GAMS gives:
- $k_A = 3925.4457 \ dm^{-3}$
- $Y_A = 3.0664 \ \mu m$

- By trial and error, these two values best fit the data.

For process B:
Take the initial value, $N_B(L = 5.4) = 1731.4 \ dm^{-3}$
Take a value from the end of the data set, $N_B(L = 26.7) = 3294.1 \ dm^{-3}$

Formulate the two equations,

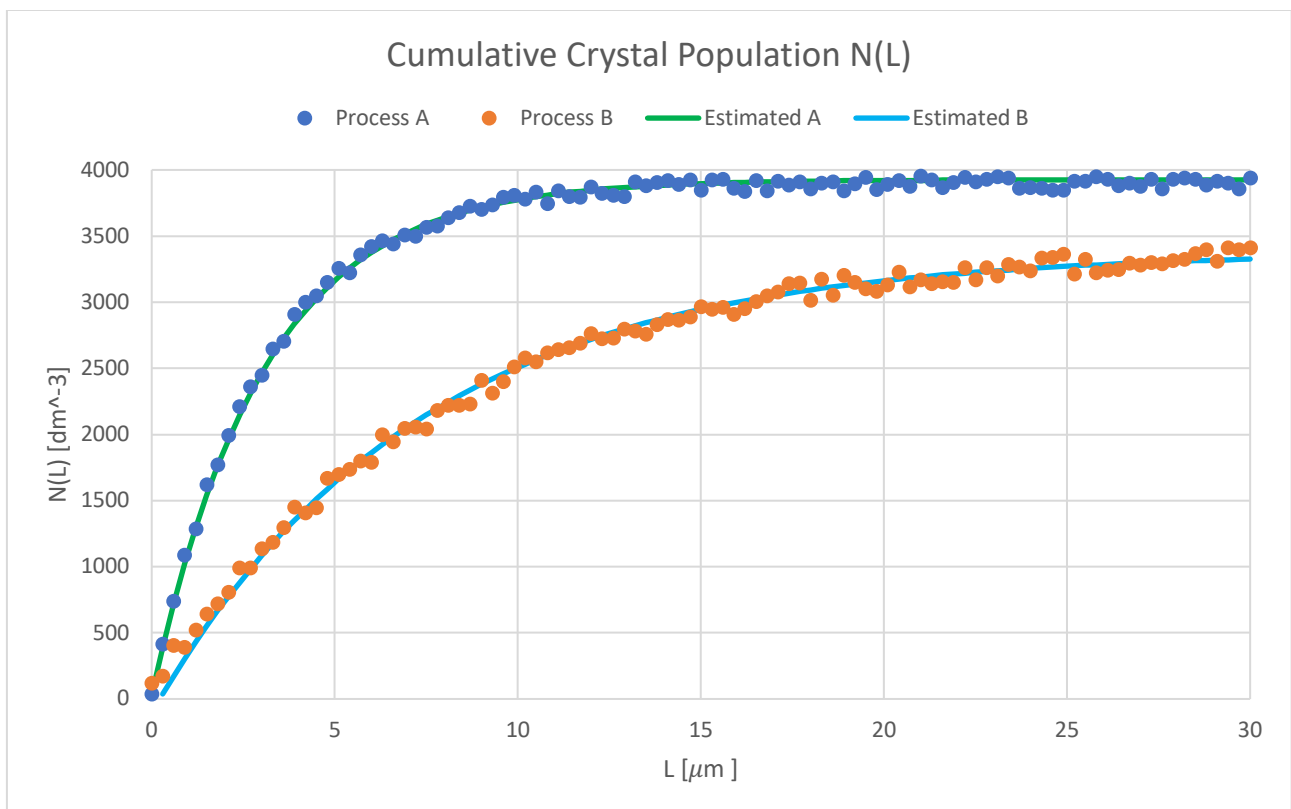$$-(482.8167) \cdot Y_B \cdot \exp\left(-\frac{5.4}{Y}\right) + k_B = 1731.4 \qquad \text{(Eq. 1)}$$

$$-(482.8167) \cdot Y_B \cdot \exp\left(-\frac{26.7}{Y}\right) + k_B = 3294.1 \qquad \text{(Eq. 2)}$$

Solving in GAMS gives:
- $k_B = 3380.2863 \ dm^{-3}$
- $Y_B = 7.2171 \ \mu m$

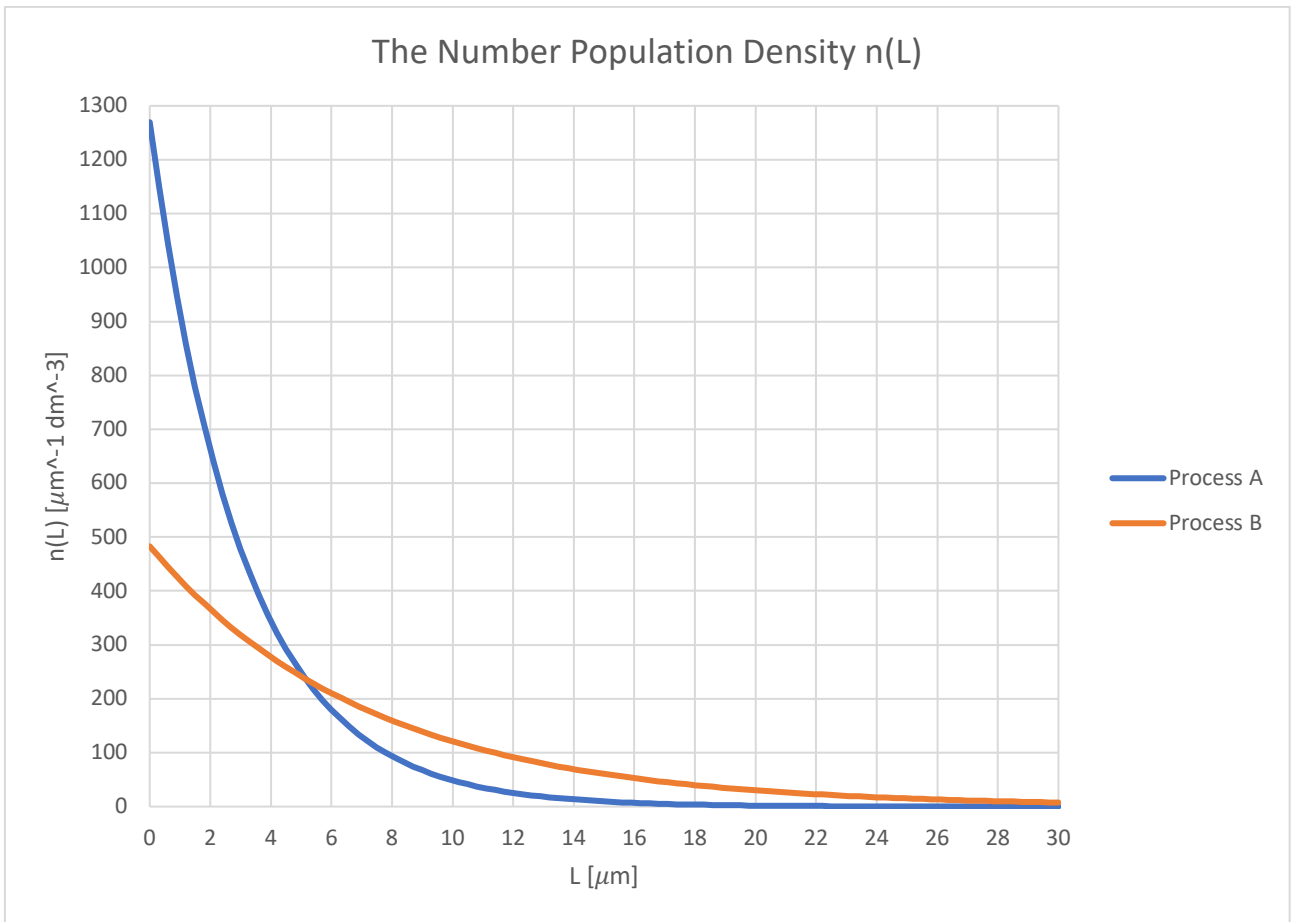- By trial and error, these two values best fit the data.

As can be seen from the figure below, the two theoretical equations using the estimated parameters fit the experimental data reasonably well:

Now we can use the parameters and plot the number density using:

$$n(L) = n_0 \cdot \exp\left(-\frac{L}{G\tau}\right) = n_0 \cdot \exp\left(-\frac{L}{Y}\right)$$

This is plotted for both processes on the figure below.

From the number density we can find all the rest.

The total length of particles per unit volume of liquid phase with size smaller or equal than size L is given by:

$$L_{tot}(L) = \int_0^L Ln \cdot dL = \int_0^L L\left(n_0 \cdot \exp\left(-\frac{L}{Y}\right)\right) \cdot dL$$

Integrating by parts:

$$\int u\,dv = uv - \int v\,du$$
$$u = L \rightarrow du = 1$$

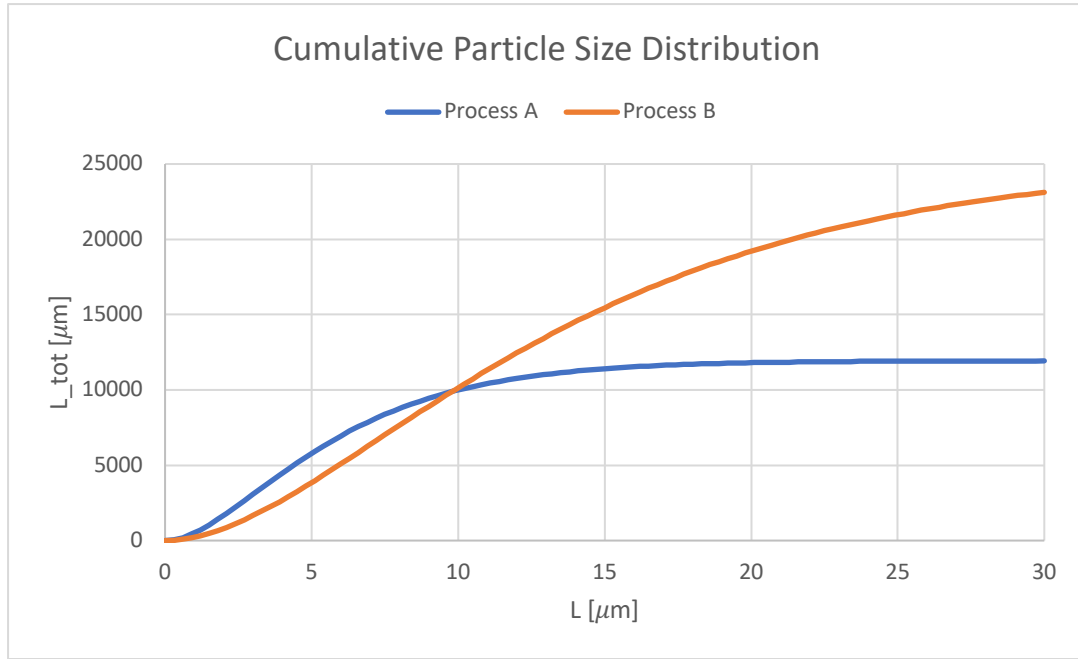$$dv = n_0 \cdot \exp\left(-\frac{L}{Y}\right) \rightarrow v = -n_0 Y \cdot \exp\left(-\frac{L}{Y}\right)$$

$$\int L\left(n_0 \cdot \exp\left(-\frac{L}{Y}\right)\right) \cdot dL = -Ln_0 Y \cdot \exp\left(-\frac{L}{Y}\right) - \int -n_0 Y \cdot \exp\left(-\frac{L}{Y}\right) dL$$

$$\rightarrow \int_0^L L\left(n_0 \cdot \exp\left(-\frac{L}{Y}\right)\right) \cdot dL = \left[-Ln_0 Y \cdot \exp\left(-\frac{L}{Y}\right) - n_0 Y^2 \cdot \exp\left(-\frac{L}{Y}\right)\right]_0^L$$

Expanding and rearranging, we obtain the final expression for the total length:

$$L_{tot}(L) = n_0 Y^2 - n_0 Y \cdot (L + Y) \cdot \exp\left(-\frac{L}{Y}\right)$$

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Plotting L_{tot} vs L for both processes gives:

Cumulative Particle Size Distribution

The total area of particles per unit volume of liquid phase with size smaller or equal than size L is proportional to:

$$A \propto \int_0^L L^2 n \cdot dL = \int_0^L L^2 \left(n_0 \cdot \exp\left(-\frac{L}{Y}\right) \right) \cdot dL$$

Integrating by parts:

$$\int u dv = uv - \int v du$$
$$u = L^2 \rightarrow du = 2L$$

$$dv = n_0 \cdot \exp\left(-\frac{L}{Y}\right) \rightarrow v = -n_0 Y \cdot \exp\left(-\frac{L}{Y}\right)$$

$$\rightarrow \int L^2 \left(n_0 \cdot \exp\left(-\frac{L}{Y}\right) \right) \cdot dL = -L^2 n_0 Y \cdot \exp\left(-\frac{L}{Y}\right) + 2Y \int L \left(n_0 \cdot \exp\left(-\frac{L}{Y}\right) \right) dL$$

From before:

$$2Y \int L \left(n_0 \cdot \exp\left(-\frac{L}{Y}\right) \right) \cdot dL = -2L n_0 Y^2 \cdot \exp\left(-\frac{L}{Y}\right) - 2 n_0 Y^3 \cdot \exp\left(-\frac{L}{Y}\right)$$
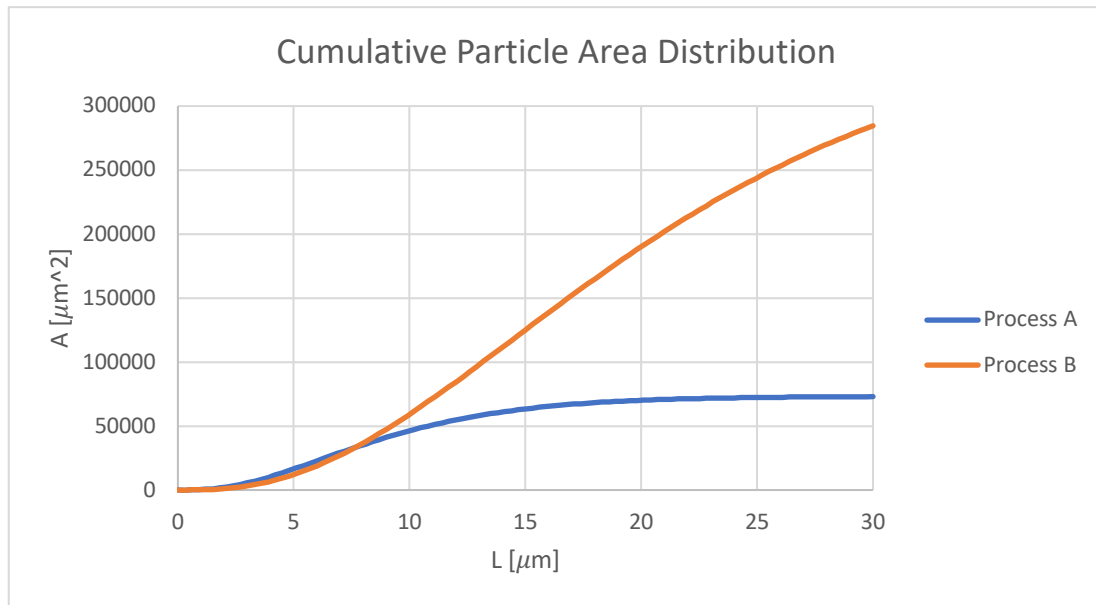
Therefore:

$$\int_0^L L^2 \left(n_0 \cdot \exp\left(-\frac{L}{Y}\right) \right) \cdot dL = \left[-L^2 n_0 Y \cdot \exp\left(-\frac{L}{Y}\right) - 2L n_0 Y^2 \cdot \exp\left(-\frac{L}{Y}\right) - 2 n_0 Y^3 \cdot \exp\left(-\frac{L}{Y}\right) \right]_0^L$$

Expanding and rearranging, we obtain the final expression for the area:

$$A(L) \propto 2 n_0 Y^3 - n_0 Y \cdot (L^2 + 2LY + 2Y^2) \cdot \exp\left(-\frac{L}{Y}\right)$$

Plotting the expression above we obtain the cumulative particle area distribution shown in the figure below:

The normalized mass distribution is the cumulative mass of crystals of size smaller than or equal to size L, as a fraction of the total, using dimensionless crystal size (x), is given by:

$$M(x) = \frac{M(L)}{M_T} = \frac{\int_0^x x^3 \exp(-x)\, dx}{\int_0^\infty x^3 \exp(-x)\, dx} = 1 - \left(1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3\right)\exp(-x)$$

- where $x = \dfrac{L}{G\tau} = \dfrac{L}{Y}$

A graph resulting from plotting this adimensional mass distribution for both processes results in a figure below:
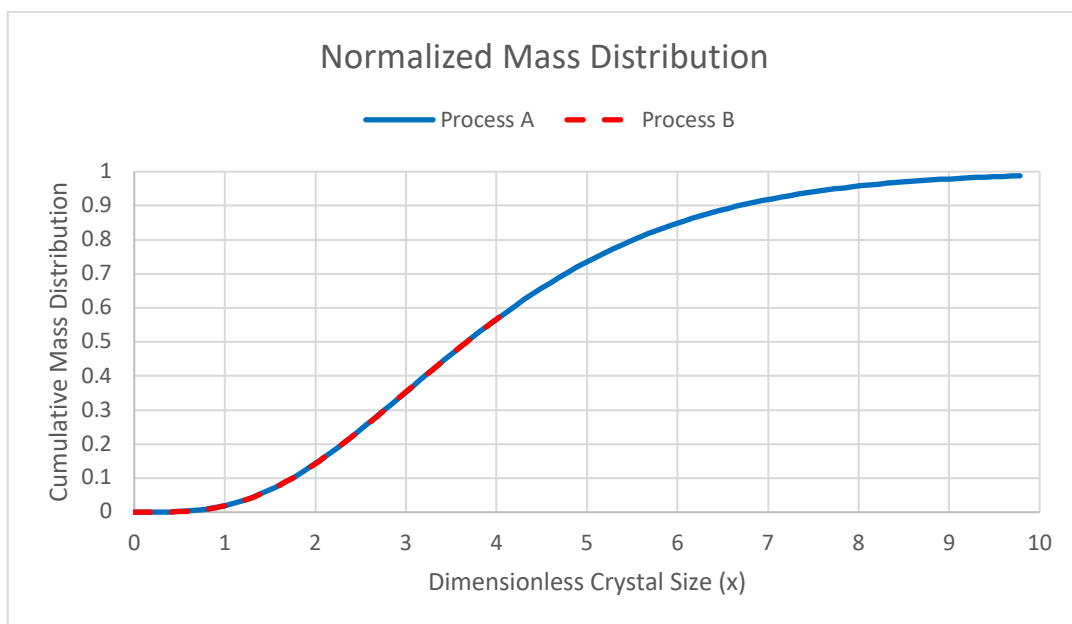
As expected, the two curves coincide with each other.

(b) Compute the dominant length L_D obtained from both processes.

The most probable, often referred to as the modal or dominant particle size, corresponds to the peak of the differential-mass distribution, and is given by:

$$L_D = 3G\tau = 3Y$$

Therefore, for Process A:

$$L_{D,A} = 3Y_A = 3 * 3.0664 = 9.199 \ \mu m$$

Similarly, for Process B:

$$L_{D,B} = 3Y_B = 3 * 7.2171 = 21.65 \ \mu m$$

(c) Can you say anything about the residence time in the two crystallizers?

The growth rate is known to be independent from both temperature and composition (i.e., $G = const$), therefore, $G_A = G_B$, and hence:

$$\frac{Y_B}{Y_A} = \frac{G\tau_B}{G\tau_A} = \frac{\tau_B}{\tau_A} = \frac{7.2171}{3.0664} = 2.3536$$

→ The residence time of Process B is about 2.4 times larger than the residence time of Process A.

(d) Which process is operating at the highest temperature?

The nucleation rate J instead depends exponentially on the inverse of the temperature through an Arrhenius-like expression:

$$J = A\exp(-B/T)$$

- where A and B are constants

Also,

$$J = n_0 G$$

$$\rightarrow \frac{J_A}{J_B} = \frac{n_{0,A}G}{n_{0,B}G} = \frac{n_{0,A}}{n_{0,B}} = \frac{1269.6133}{482.8167} = 2.6296$$

Then,

$$\frac{J_A}{J_B} = \frac{A\exp(-B/T_A)}{A\exp(-B/T_B)} = \exp\left(\frac{B}{T_B} - \frac{B}{T_A}\right) = 2.6296$$

Rearranging we obtain:

$$\frac{B}{T_B} - \frac{B}{T_A} = \ln(2.6296) = 0.9668 \ (i.e., +ve)$$

Therefore,

$$\frac{B}{T_B} > \frac{B}{T_A} \rightarrow T_A > T_B$$

→ This shows that Process A is operating at a higher temperature than Process B.