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SELECTIVE FINES DESTRUCTION IN BATCH CRYSTALLIZATION

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SELECTIVE FINES DESTRUCTION
IN BATCH CRYSTALLIZATION

by
Gail Lea Zipp

A Thesis Submitted to the Faculty of the
DEPARTMENT OF CHEMICAL ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
In the Graduate College
THE UNIVERSITY OF ARIZONA

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ABSTRACT

Batch crystallization of pentaerythritol was carried out with and without fines destruction to determine the effects of fines destruction on the CSD (crystal size distribution). Population balance equations were then used to predict the experimentally observed CSD changes. Batch growth rate experiments were conducted to determine the kinetics of pentaerythritol growth.

INTRODUCTION

The purpose of this study was to determine the effect of fines destruction in a batch crystallization system. Fines destruction has been shown to improve the crystal size distribution (hereafter referred to as CSD) in a continuous crystallizer. However, to date only one study has been presented for the batch case.

In most systems, the final CSD is an important consideration. An increase in the average crystal size and a reduction in the number of small crystals will increase filtration rate, lower the amount of mother liquor entrained on the crystals and possibly increase the value of the product. The results of this study show that the application of fines destruction in a batch crystallization system improved the final CSD.

Fines destruction increases the operating cost of a batch crystallizer due to the additional cooling load caused by the returning fines stream. Therefore application of this technology is best suited to low volume high cost chemicals where the additional operating expense would be small compared to the increased value of the final product.

Pentaerythritol, abbreviated as PE, was used as the substance for crystallization. It was chosen because it has a large solubility versus temperature dependence, is non-toxic and is relatively inexpensive.

PE was crystallized in a batch crystallizer with and without fines destruction. The runs were identical in all other ways. Changes in the final CSD were then directly attributed to the presence of fines destruction.

Growth rate experiments were performed at 65°C and 55°C to measure growth dependence on supersaturation and temperature. The results were compared to those previously reported by Rogers and Creasy (1974) and Clatworthy, Rehmatullah, Wahab and Creasy (1976).

Three batch experiments were conducted to monitor changes in CSD with time. Two were with fines destruction and one was without. The results were compared with those predicted using the population balance CSD analysis.

THEORY

Population Balances

The general population balance developed by Randolph and Larson (1971) is written for a batch crystallizer as

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial L} = 0 \quad (1)$$

where $n(L)$ is the population density of crystals at size L and G is the linear growth rate. The boundary condition for Equation (1), $n(0,t)$, is related to the nuclei population density at $L=0$, n^0 , and to the nucleation rate, B^0 , as

$$n^0(0,t) = n^0(t) = B^0(t)/G(0,t) \quad (2)$$

The initial condition for Equation (1) is more difficult to define. If seed crystals are added to the crystallizer at time $t=0$, the initial population density distribution may be represented by the population density distribution of the seed crystals, $n_s(L)$. For systems that are not seeded, the initial distribution formed by nucleation mechanisms is not precisely known. For this case Baliga and Larson (1970) suggest using the crystal population density distribution present when crystals first appear in the system.

Batch Processes

Batch crystallization processes are usually divided into two types: cooling and evaporative. In this discussion only crystallization by cooling is considered. However, the equations developed will be similar for other batch processes.

Substances which can be crystallized by cooling are characterized by large changes in solubility with temperature. For example, the solubility diagram of Pentaerythritol is shown in Figure 1. At a temperature of 75°C (point A) the PE equilibrium concentration is 359kg/m³. In most batch processes, the solution is cooled to a temperature below the saturation temperature (point B) to create a supersaturated solution. The supersaturation of this solution can be expressed in several ways, the two most common are:

$$s = C_{PE} - C_{PE}^*$$

$$S = \frac{C_{PE}}{C_{PE}^*} \quad (3)$$

where: C_{PE} = Concentration of PE (kg/m³)
 C_{PE}^* = Saturation concentration of PE (kg/m³)

Figure 1 Pentaerythritol Solubility Diagram.

At point B, the temperature is 70°C, the equilibrium concentration, C^* , is 299kg/m³ and the supersaturation of the solution, s , is 60kg/m³ or S is 1.201. If the temperature is held constant and seed crystals are added, they will grow and eventually deplete the solution of all supersaturation. This corresponds to a movement from point B to point C. At this time the total mass of the crystals will have increased an amount equivalent to the change in concentration of the solution. For this case the solid mass would be 60kg/m³.

This process could theoretically be repeated until all PE was depleted from the solution. However, kinetics also play an important role. The growth rate of crystals is usually represented by the empirical relationship:

$$G = k_g S^a \quad (4)$$

with: $k_g = k \exp(-E_a/(R T))$

where:

- G = linear growth rate
- k_g = growth rate constant
- S = supersaturation
- a = supersaturation exponent
- k = pre-exponential constant
- E_a = activation energy of crystallization
- R = gas constant
- T = temperature

The growth rate of the crystals added at point B will decrease as the supersaturation is reduced. Also, the

same crystals will take longer to deplete the same amount of supersaturation from point B' to C' than from B to C because the temperature is lower.

In batch crystallization operations the procedure is not one of decreasing the temperature, waiting for equilibrium and repeating the procedure but rather one of continually decreasing the temperature to provide new supersaturation for crystal growth. The best method would then seem to be to decrease the temperature rapidly to maintain as high a supersaturation as possible. However, there are other constraints on the system.

Crystals will spontaneously form in a solution if the supersaturation exceeds the metastable zone. This occurs due to primary nucleation. Thus, the solution cannot be cooled too rapidly or the metastable zone would be exceeded and the solution would spontaneously nucleate. Although the same mass of crystals would be obtained from the solution, the number and crystal size distribution would be vastly different.

Another consideration is the crystal area available for growth. Initially, when the seed crystals are added, the total area is small. Because of this, the initial cooling rate must be slow. Otherwise, the supersaturation will exceed the nucleation limit and primary nucleation will occur. As the seed crystals grow, their area increases and

therefore the cooling rate can be increased. However, because the growth rate has an Arrhenius temperature dependence the cooling rate should decrease as the temperature decreases. Thus, during the progression of the batch crystallization process the optimum cooling rate is influenced by the available crystal area and the temperature of the system.

Qualitatively the optimum cooling curve should begin with rapid cooling close to the primary nucleation limit. The seed crystals would then be added and the solution cooled slowly. The cooling rate would then be adjusted to maintain a high and approximately constant supersaturation and thus a high growth rate. An optimum cooling curve is shown in Figure 2. This temperature versus time curve is almost the opposite of the temperature profile that would occur if cooling were allowed to take place naturally.

Optimum Cooling Curves

Several methods are available for determining the optimum cooling curve for a batch crystallization process. In all of them it is necessary to know the temperature dependence of solubility and growth rate and the nucleation limits.

Larson and Garside (1973) and Mullin and Nyvlt (1971) have demonstrated different methods to obtain an optimum cooling curve given a known maximum growth rate.

Figure 2 Optimum and Natural Cooling Curves.

A similar form of the cooling curve is obtained in both methods. The non-dimensional temperature varies with time as

$$-\frac{d\theta'}{dZ} = Z^2 + 2Z + 1 \quad (5)$$

where θ' = Non-dimensional temperature
 Z = Non-dimensional time

A third method of determining an optimum cooling curve is a graphical approach. White (1984) demonstrated how this approach could be used to predict the yield of a continuous precipitator train. The method can be modified to apply to a batch system as follows.

Given the form of the growth rate, G , and an equation predicting the solubility (saturation concentration), the maximum growth rate can be calculated for any concentration and temperature by substituting the solubility equation into the growth rate equation and setting the derivative equal to zero.

For example, solving

$$\left. \frac{\partial G}{\partial t} \right|_{x_{PE}} = 0$$

where G = growth rate

t = temperature

and x_{PE} = PE mass fraction in solution

will result in an equation determining the optimum solution composition necessary at a given temperature to obtain the maximum growth rate. If the optimum solution concentration is greater than the nucleation limit, the maximum growth rate possible is calculated at the nucleation limit.

Fines Destruction

Following an optimum cooling curve has been shown to improve the final CSD compared to that which was obtained by natural cooling (Mullin and Nývlt(1971)). However, in agitated vessels, crystal formation due to secondary nucleation has been shown to occur when the supersaturation is below the primary nucleation limit. Thus all growth will not occur on the seed crystals and the final CSD will be wider.

Secondary nucleation is typically the mechanism of particle formation in continuous mixed magma crystallizers. The CSD can often be improved by including a fines withdrawal stream as demonstrated by Randolph and Larson, Chapt. 8 (1971) and Juzaszek and Larson (1977). Fines destruction has also been shown to improve the final CSD in a batch crystallizer (Jones, Chianese and Mullin (1984)). A fines destruction loop withdraws a classified slurry from the crystallizer which contains only crystals below a cutoff size L_F . The fines stream is then heated to dissolve the

crystals and returned to the crystallizer. Thus, the number of small crystals is reduced but their dissolved mass is returned for additional growth of the large crystals.

A fines trap, shown in Figure 3, is the mechanism used to remove the classified suspension of fines. As fluid is drawn into the fines trap, larger crystals settle out of the trap before being carried out of the crystallizer. Crystals that settle at the same velocity or less than the upward velocity of the stream in the fines trap are carried out of the crystallizer and dissolved.

An estimate of the cutoff size to be removed can be made by using Stokes law of settling. This can be checked by measuring the actual size removed with different flow rates.

Figure 3 Fines Trap.

Effect of Fines Destruction on CSD

The effect of a fines destruction loop on the CSD of a batch crystallizer can be predicted by adding removal terms to the population balance equation. Equation (1) then becomes:

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial L} + \frac{Q(L)}{V} n = 0 \quad (7)$$

where

$$\frac{Q(L)}{V} = 0; L > L_F$$

$$\frac{Q(L)}{V} = h; L \leq L_F$$

and

h = fines removal frequency

$Q(L)$ = fines removal rate, m^3/s

V = crystallizer volume, m^3

Jones, et al.(1984) numerically solved Equation (7) with equations for kinetics and solubility to determine the final CSD of potassium sulphate.

Predicting the Effect of Fines Destruction on CSD

A predictive method for determining changes in CSD due to fines destruction is presented here. In it, the following assumptions are made:

- 1) The crystallization is carried out with an ideal cooling curve such that the growth rate is constant.
- 2) No nucleation occurs.
- 3) There is no size dependence or dispersion of the growth rate.

In a seeded batch crystallizer, at a given moment, the population distribution of crystals would be as shown in Figure 4. In a small time span, Δt , the crystals grow with the increase in crystal size given by:

$$\Delta L \approx G \Delta t$$

The change in the population density distribution due to growth is shown in Figure 4. After the crystals have grown, and within the time span Δt , a fraction of crystals smaller than size L_F are destroyed. This would not change the population density of crystals that were larger than L_F at the beginning of the time period. Thus, point A still becomes A' and the population density of crystals larger than L_F is not changed by fines destruction (the dark line).

Crystals smaller than $L_F - \Delta L$ at the beginning of the time period will be destroyed at the frequency h . Their population density will be correspondingly reduced. Point B would become B' due to crystal growth. However, fines destruction reduces the population density and it becomes B''.

Crystals between the sizes of $L_F - \Delta L$ and L_F at the beginning of the time period Δt will have a changing frequency of removal. Crystals slightly smaller than L_F will have a short time of exposure to fines destruction

Figure 4 Population Density Changes Due to Fines Destruction.

before they grow larger than L_F and their population density will be reduced little. On the other hand, crystals that are slightly larger than $L_F - \Delta L$ will be exposed to fines destruction close to the entire time period Δt . Their population density will be reduced by a factor close to that for crystals smaller than $L_F - \Delta L$ at the beginning of the time period.

The population density at any time $t + \Delta t$, is then represented as:

$$n(L)_{t+\Delta t} = n(L - \Delta L)_t \phi(L) \quad (8)$$

with the function $\phi(L)$ that defines the change in population density given as:

$$\begin{aligned} \phi(L) &= \exp(-\alpha) & L < L_F - \Delta L \\ \phi(L) &= \exp\left(\alpha \left(\frac{L_F - L}{\Delta L}\right)\right) & L_F - \Delta L < L < L_F \\ \phi(L) &= 1 & L > L_F \end{aligned}$$

where $\alpha = (Q_F / V) \Delta t$
 - the number of turnovers in time period Δt

Equation (8) can be used to predict the change in CSD in a batch crystallizer due to fines destruction.

Batch Growth Rate Determination

Misra and White (1971) present a convenient method of evaluating crystal growth rates using changes in the cumulative number distribution.

The general population balance, Equation (1), is written for the case of no nucleation, agglomeration or breakage in terms of cumulative numbers as:

$$\frac{\partial(NF)}{\partial t} = -NG \frac{\partial(F)}{\partial(L)} \quad (10)$$

where N = the total number of crystals, $\#/m^3$

F = the cumulative percentage of crystals smaller than size L

and the growth rate on seed crystals is given by

$$G = \left. \frac{\partial L}{\partial t} \right|_F \quad (11)$$

Using Equation (11) the growth rate can be evaluated as the change in size of crystals during a time period Δt at a constant cumulative number; that is,

$$G \approx \left. \frac{\Delta L}{\Delta t} \right|_F \quad (12)$$

Equation (12) is based on a cumulative distribution of crystals smaller than a given size. Unfortunately, size analysis methods are limited to a minimum measurable size and the actual number of crystals smaller than a given size NF , and the total number of crystals N , are not known. However, the total number of crystals larger than a given size $N(1 - F)$, can be measured directly from particle

counter results or by conversion of sieve analysis mass data to number data. If F is constant, the value of $N(1 - F)$ will be constant and Equation (12) is still valid. The procedure can be used if nucleation occurs, provided the seed crystals can be distinguished from crystals formed by nucleation. An example of the analysis is shown in Figure 5.

Figure 5 Determination of Growth Rate from CSD Changes.

EXPERIMENTAL PROCEDURE

The procedure for all experimental work completed is detailed below. A summary of experimental runs is given in Table 1.

Cooling Curve Determination

The cooling curve used for the batch crystallization experiments of PE was determined based on the optimum cooling principles discussed in the previous section. However, because PE crystallization kinetics were not known at the beginning of the experimentation, it was not possible to have an analytically determined cooling curve. Therefore, knowing that slow initial cooling and rapid final cooling were necessary, a cooling curve was chosen *a-priori* that met those requirements. Initial and final temperatures of the batch solution were chosen in such a manner that a reasonable temperature span was covered, the solution concentration would be reduced by a significant amount and published saturation data could be used.

The cooling curve chosen is shown in Figure 6. It is probably not the optimum cooling curve for the PE water system. However, if the same curve is used, the results of runs conducted using it while varying some other parameter (such as fines destruction) can be compared and changes

attributed to the parameter varied rather than the cooling curve.

Table 1
Summary of Runs

Run #	Run Date	Fines Destruction	Run Type
1	9-5-85		Effect of fines destruction on final CSD, seeded
2	9-10-85		
3	9-13-85		
4	9-16-85		
5	9-23-85		
6	9-25-85	✓	
7	9-26-85	✓	
8	10-01-85	✓	
9	10-02-85	✓	
10	12-02-85		
11	12-03-85		
12	12-18-85	✓	
13	4-21-86		Effect of fines destruction on final CSD, non-seeded
14	4-22-86	✓	
15	4-23-86		
16	4-29-86		
17	5-09-86	✓	
18	5-08-86	✓	Effect of fines destruction on the transient CSD
19	7-02-86		
20	7-09-86	✓	
21	5-05-86		Growth rate at 65°C
22	5-15-86		
23	6-13-86

Figure 6 Cooling Curves Used for Batch Crystallization Experiments.

Effect of Fines Destruction on the Final CSD:
Seeded Batch Crystallization Experiments

Runs #1-12 were conducted with an initial pentaerythritol concentration of 358kg/m^3 . This corresponds to a saturation temperature of 75°C . In most cases, the solution was made by adding 2330 grams of PE to 6.5 liters of filtered ($25\mu\text{m}$) distilled water to produce a final volume of approximately 8 liters. For some runs, sufficient PE was added to the solution remaining from a previous run to increase its concentration to 358kg/m^3 .

This solution was heated in the crystallizer to approximately 80°C while stirring until all crystals were dissolved. The solution was then rapidly cooled to 70°C and the programmed cooling curve followed.

Seed crystals consisting of two grams of crystals in the $177\text{-}250\mu\text{m}$ range saved from previous runs were added to the tank when the temperature reached 70°C . The seed crystals were first placed in a separatory funnel containing approximately 20 ml of a 16°C saturated PE water solution. This was done to dissolve any small crystals attached to the seeds and prevent nucleation. After approximately ten minutes, the slurry was added to the crystallizer and crystals remaining in the separatory funnel were washed into the crystallizer with an additional 10 ml of PE solution.

For runs without fines destruction, the tank was insulated with fiberglass insulation. This was necessary as

heat losses through the tank walls caused the solution temperature to drop faster than the programmed cooling curve. For runs with fines destruction, the insulation was not used as heat input from the returning dissolved fines stream compensated for the loss through the walls.

For runs with fines destruction, the fines trap was placed between the wall of the crystallizer and the draft tube (see Figure 7). Once the crystallizer was heated and all crystals were dissolved, the fines pump removing the fines stream was turned on. The fines removal rate was calibrated by diverting the fines return stream into a graduated cylinder and measuring the volume of fluid pumped in a given amount of time. The pump rate was then adjusted and the flow rate measured until the desired setting was reached. The fines pump was left running while the solution was rapidly cooled and during the usual cooling curve. After the run was finished, the rate of fines removal was measured again and the average of the two readings used as the removal rate for the run.

The temperature of the hot water bath used to heat the fines stream was set at 90°C.

At the end of the batch time a sample was withdrawn from a side sample port into a graduated cylinder. The total volume of the sample was measured, the crystals filtered on a glass frit filter and the clear liquor set

Figure 7 Schematic Diagram of the Crystallizer.

aside for later volume measurement. The crystals were washed with room temperature methanol saturated with PE and filtered. After air drying, the total mass of the crystals was measured and the crystals sieved using an Allen-Bradley® sonic sifter. Sieve fractions were then weighed and this data used for calculations.

Effect of Fines Destruction on the Final CSD:
Non-seeded Batch Crystallization Experiments

Runs #13-18 were conducted exactly as the batch experiments discussed above with one major exception, seed crystals were not added. The solution preparation was not changed nor was remainder of the procedure. After dissolving all crystals the solution was rapidly cooled to 70°C and the usual cooling curve followed. At the end of the batch time, a sample was withdrawn from the side sample port and analyzed as stated above.

Transient Changes in CSD
due to Fines Destruction

Runs #19-21 were conducted in a manner similar to the non-seeded batch experiments. The cooling curve followed for Run #19 was the same as used for all previous runs. For Runs #20 and 21 the second cooling curve shown in Figure 6 was used.

Solid and liquid samples were taken throughout each run to determine changes in supersaturation and crystal size

distribution with time. As many samples as possible were taken during each run, their number being limited by the ability of the experimenter to take them.

Solid Samples

Solid samples were withdrawn through the side sample port directly onto a weighed preheated (40-60 μ m pore size) glass frit filter arrangement. The sample was filtered as it was taken. After collecting approximately two grams of solid sample on the filter the vacuum was removed and the total weight of the sample measured. The solid sample was then washed with ethanol (which was heated to the current crystallizer temperature and saturated with PE), vacuum dried and weighed.

The sample was then analyzed in two parts. First, it was sieved using the sonic sifter. Screen sizes down to 150 μ m were used. The portion of the sample smaller than 150 μ m was saved and analyzed using the PDI particle counter. This was done by suspending all or a portion of the remaining crystals in a conducting solution and measuring the particle size distribution with a PDI Elzone® particle counter.

Liquid Samples

Liquid samples were withdrawn through a hole in the lid of the crystallizer. A preheated syringe filter

containing a $5\mu\text{m}$ pore size filter was attached to a 10ml syringe. The sample was withdrawn into the syringe through a tube attached to the filter. The filter arrangement was then removed and the syringe containing the liquid sample weighed. The sample was then ejected into a plastic bottle containing a known amount of distilled water and the syringe weighed again. Occasionally, if the supersaturation was very high, the liquid sample in the syringe would nucleate and some solid material would be left inside the syringe after ejecting the sample into the bottle. In this case, before weighing the syringe, liquid from the bottle would be drawn into the syringe and ejected several times to rinse the crystals out.

The refractive index of the diluted sample was measured at 30°C . The actual solution concentration was then calculated using the appropriate dilution factors.

Calibration of PDI Particle Counter

A PDI Elzone[®] particle counter was used to analyze crystals smaller than $150\mu\text{m}$. Methanol containing 2% lithium chloride was used as the electrolyte solution. This was necessary as the solubility of PE in water changes considerably with temperature.

Initial Settings

The orifice size used was $380\mu\text{m}$. Thus, the range of sizes to be measured was 2-40% of orifice diameter or 7.6 to $152\mu\text{m}$. The log setting used for this orifice was 12.

Particles of $44.6\mu\text{m}$ diameter with a narrow size distribution were used to calibrate the PDI. First, the particles were added to a conductive solution and the current and gain adjusted such that the gain was minimized and the current maximized without causing boiling at the orifice. The channel corresponding to the peak in the calibration particle distribution was noted for those settings. The gain was then changed to create "hypothetical" particles of a different diameter. The channel containing the peak number of counts for those hypothetical particles was assigned to the diameter of the hypothetical particles. The gain was changed again and channel verses size recorded. This procedure was repeated with $19.0\mu\text{m}$, $20.4\mu\text{m}$, and $40.3\mu\text{m}$ diameter particles.

Calibration by Mass Balance

The calibration of the PDI was checked by a mass balance. PE crystals were sieved and those in a small size range saved. A known mass of this sample was then added to a measured amount of electrolyte solution to make a suspension with a known slurry density, M_t . The mixture was analyzed with the particle counter and the M_t calculated from the measured crystal size distribution using the density of PE and appropriate population density equations.

Other Calibration: Refractometer

The refractive index of various dilute PE solutions was measured at 30°C. The solutions were made by dissolving a pre-weighed amount of PE in a known amount of filtered distilled water. The measured refractive index, n_d , was recorded for each solution and the best straight line through the data points used.

Growth Rate Experiments

Growth Rate Experiments at 65°C

Runs #22 and 23 were conducted at 65°C. A mixture of PE and filtered distilled water with a PE concentration of 358kg/m³ was heated to 80°C to dissolve all crystals. It was then quickly cooled to 65°C and the temperature held constant. After the solution nucleated solid sampling was

started. Both liquid and solid sampling procedures were as described for Runs #19-21.

Growth Rate Experiment at 55°C

The procedure for the growth rate experiment at 55°C was similar to the 65°C run. The initial solution had a PE concentration of 281kg/m³. After heating the solution to dissolve all crystals, the solution was rapidly cooled to 55.4°C, the temperature held constant and sampling started.

Determination of Particle Size versus Rate of Removal

After a batch crystallization run, the crystallizer was allowed to cool naturally to room temperature while stirring at 450RPM. The fines trap was then installed in its usual position in the crystallizer and the fines pump started. The fines stream was returned directly to the crystallizer and not heated. After measuring the rate of fines removal, the return fines stream was diverted onto a glass frit filter, vacuum filtered and washed with ethanol. After drying, the crystals were sieved and the largest screen with a significant mass of crystals noted. This procedure was then repeated for several removal rates.

EQUIPMENT

A description of equipment used for experimentation is given here. Unless otherwise noted, the same equipment was used for all experiments.

Crystallizer

Clear cast acrylic was used for the crystallizer and draft tube. This aided in the visualization of flow and circulation patterns. The tank was constructed by using methylene chloride to glue a circular piece of acrylic to one end of a piece of clear cast acrylic tubing. The bottom was then further shaped by heating the tank and using a metal rod to press the middle towards the inside thus forming a "bump". The corners were filled in and contoured with clear bathtub caulk. Both modifications were performed to improve the circulation of fluid in the tank. Figure 7 is a schematic of the crystallizer.

The draft tube was a length of clear cast acrylic tubing. Baffles were formed by gluing pieces of clear acrylic to the sides of the tube. The baffles extended below and above the draft tube to the bottom and top of the tank.

The sample port was constructed by drilling and tapping a hole in the side of the crystallizer. A plastic

fitting was then screwed into the hole from the inside. The threads of it extended sufficiently beyond the outer wall of the crystallizer to attach another plastic fitting. The outside fitting provided an attachment location for tubing through which the samples could be directed. During a crystallization run, the tubing was clamped off at all times except when samples were taken.

The inner plastic fitting was "L" shaped. Its opening pointed down and was centered between the draft tube and the tank wall. The shape of the fitting was chosen to provide isokinetic removal of solid samples.

The lid of the crystallizer was also clear acrylic plastic. Small plastic pieces glued to the bottom of it fit tightly inside the crystallizer and kept it in place during runs. Holes were drilled in it for the cooling coil, temperature probe and liquid sample access. When any opening was not in use it was sealed to minimize evaporative losses.

Cooling System

The crystallizer was cooled by flowing a cold water-antifreeze solution through a stainless steel coil located inside the draft tube. A schematic of the entire cooling system is shown in Figure 8. The water-antifreeze solution was stored in the tank and cooled with an immersion cooling coil prior to a run. During a crystallization experiment,

Figure 8 Schematic Diagram of the Cooling System.

cold fluid was pumped continuously from the tank through a normally open valve and returned to the storage tank. When the temperature of the crystallizer exceeded the set point temperature the controller would close the valve and direct the cooling fluid through the crystallizer before returning it to the storage tank. After the crystallizer was cooled to the desired temperature, the controller would discontinue the voltage output. The valve then opened and cooling fluid bypassed the crystallizer and returned directly to the tank.

To heat the crystallizer prior to a run the cooling system tubing was detached from the cooling coil and tubing from a hot water bath attached.

Temperature Control

The temperature of the crystallizer was controlled with a Tempstar II temperature controller. A 0.1°C RTD thermocouple probe provided input temperature information to the Tempstar II. The desired cooling curve was programmed into the Tempstar II and when the crystallizer temperature was above the set point the Tempstar II output a signal which closed the cooling water bypass valve.

Sonic Sifter

Solid samples were analyzed with an Allan-Bradley sonic sifter. In it, a series of sieve trays are arranged in increasing mesh size (decreasing average hole size). The

crystal sample is placed on the topmost sieve and sonic waves are used to vibrate the stack. The crystals fall through the holes in the sieves until they reach a sieve with a hole size smaller than the diameter of the crystal. The weight of crystals reporting to each sieve is the weight distribution of the sample. This can then be converted to cumulative number and population density distributions.

Particle Data Inc.
Particle Counter

The PDI particle counter is a zone sensing device that was used to measure crystal size distributions below $160\mu\text{m}$. In it, crystals are suspended in an electrolyte solution and drawn through a small orifice. A current is passed through the electrolyte which also must pass through the orifice. When a crystal enters the orifice region it causes a fluctuation in the current proportional to its volume. The PDI measures the current fluctuations and converts them to particle size measurements. This data is sent to a PDP 8/a minicomputer which calculates cumulative numbers of crystals larger than a given size. This data is then used to calculate population density information. A typical output of the PDP 8/a is shown in Figure 9.

AUTO-EXECUTE STRING>B

PARTICLE SIZE ANALYSIS

SAMPLE ID:--CALIB CHK SZ=#19 M=0.01155 V=500ML

LOWER TRIGGER SET AT 5 #

DATE:--2 28 86 #

PRESET STOP = 500

#

GIVE GO COMMAND WHEN READY GO

ANALYZE 8564 #FULL SAVE 2 #SMOOTH #SMOOTH #SMOOTH

CALCULATE LOG MEAN, L, MODE, M, AND MEDIAN, N OF THE SIZE DIST
CHAR 45.59 14.42 70.60 #

CALCULATE CUM ULATIVE VALUES LARGER THAN:

CUM. 001% 109.35 #CUM. 005% 104.42 #CUM. 010% 104.42

CUM. 020% 99.73 #CUM. 120% 90.95 #CUM. 220% 84.88

CUM. 040% 97.46 #CUM. 140% 88.88 #CUM. 240% 84.88

CUM. 060% 95.24 #CUM. 160% 88.88 #CUM. 260% 82.95

CUM. 080% 93.07 #CUM. 180% 86.86 #CUM. 280% 82.95

CUM. 100% 93.07 #CUM. 200% 86.86 #CUM. 300% 81.06

CUM. 520% 69.00 #CUM. 620% 54.81 #CUM. 720% 20.84

CUM. 540% 67.43 #CUM. 640% 46.65 #CUM. 740% 19.01

CUM. 560% 65.89 #CUM. 660% 35.39 #CUM. 760% 17.74

CUM. 580% 62.93 #CUM. 680% 26.85 #CUM. 780% 16.55

CUM. 600% 60.09 #CUM. 700% 23.38 #CUM. 800% 15.81

CUM. 990% 13.77 #CUM. 999% 13.46 #

READ THE COUNTS FROM THE KEYBOARD (AVERAGE OF ALL READINGS)

RCOUNT=244;CORRECTED= 122.000 #

Figure 9 Typical Output of the PDP8/a Mini-Computer.

Refractometer

A Bausch & Lomb laboratory Abbe type refractometer was used for refractive index measurements. The temperature of the prism was kept constant by attaching a constant temperature bath which circulated water at the specified temperature.

RESULTS

Effect of Fines Destruction on the Final CSD

Eighteen experiments were conducted to determine how fines destruction affects the final CSD of batch crystallized pentaerythritol. Results are presented here.

Seeded Batch Experiments

Runs #1-12 were seeded batch experiments carried out with and without fines destruction. The effect of fines destruction can be seen by comparison of the final results. Runs #1-5, 10 and 11 form the control case with no fines destruction. The cumulative number of crystals larger than a size, $N(L)$, versus size, L , is shown in Figure 10. The CSD is relatively constant because the same cooling curve was used for all seven runs.

Figure 11 shows the cumulative number of crystals larger than a size, $N(L)$, versus size, L , for Runs #6-9 and 12 in which fines destruction was included. The final CSD of the five varies with the fines destruction rate.

Sample data for all twelve runs is given in Table 2. The crystal mass, liquid volume measurements, and slurry density, M_t , is shown. Slurry density was calculated using both the total sample volume, v_t and the clear liquor volume, v_l . In both cases, the basis of the slurry density

was the same, per unit volume of clear liquor and therefore the value should be the same. However, the values are not consistent, indicating a lack of accuracy in volumetric measurements.

Figure 10 Cumulative Number Distribution of Runs #1-5, 10 and 11.

Figure 11 Cumulative Number Distribution of Runs #6-9 and 12.

Table 2
Sample Data for Runs #1-12

Run #	m_s (g)	v_t (ml)	v_l (ml)	M_t^1 (kg/m ³)	M_t^2 (kg/m ³)
1	81.7	430	(372)	220	-
2	83.9	400	335	250	247
3	85.4	455	(394)	217	-
4	89.1	433	(369)	241	-
5	92.7	445	355	261	245
6	56.4	-	360	157	-
7	60.1	405	340	177	166
8	70.5	417	320	220	192
9	53.1	312	265	200	194
10	85.8	450	360	238	221
11	88.2	440	340	259	234
12	62.4	475	395	158	145

M_t^1 calculated using v_l

M_t^1 calculated using v_t

() v_l estimated from v_t and sample mass, m_s

Non-Seeded Batch Experiments

Five experiments were conducted to determine the effect of fines destruction on a non-seeded batch crystallization of PE. The cooling curve followed was identical to the one used for the seeded batch experiments.

Runs #13, 15 and 16 did not employ fines destruction. Runs #14 and 17 were with fines destruction. The cumulative number distributions, $N(L)$ versus L , are shown for all five in Figure 12. The final CSD of the runs without fines destruction is again constant while the runs with fines destruction have a more variable final CSD.

The coil used to heat the fines stream in Run #14 was the same one used in Runs #1-12. It had only one loop while the coil used for Run #17 and for all subsequent runs had nine loops. The greater heat transfer area and longer residence time of the second coil will affect the dissolution of the crystals in the fines stream and increase the reduction of small crystals.

The measured slurry density, M_t , calculated from v_t and v_1 for all six runs is shown in Table 3. The calculations have the same basis of unit volume of clear liquor. However, the results are not consistent, again indicating a lack of accuracy in volumetric measurements.

Figure 12 Cumulative Number Distribution of Runs #13-17.

Table 3
Slurry Density Calculations
Runs 13-17

Run	m_s (g)	m_t (g)	v_t (ml)	v_l (ml)	M_t^1 (kg/m ³)	M_t^2 (kg/m ³)
13	71.08	-	405	295	201	241
14	94.43	-	433	337	258	280
15	58.7	-	314	245	216	240
16	84.4	460.5	-	350	231	241
17	7.06	54.0	-	-	155	-
18	36.83	217.4	-	-	210	-

M_t^1 calculated using v_t or m_t

M_t^2 calculated using v_l

Transient Changes in CSD
due to Fines Destruction

The CSD and supersaturation of three batch experiments were monitored with time to determine the transient effects of fines destruction and to provide data for comparison with the predicted CSD changes. Runs #18 and 20 were conducted with fines destruction, Run #19 was without fines destruction.

The supersaturation was monitored to determine the performance of the chosen cooling curve.

Figures 13 and 15 present the cumulative number larger than size L , $N(L)$, results of Run #18 and #20. Both figures clearly demonstrate how fines destruction reduces the number of crystals smaller than $150\mu\text{m}$. The $N(L)$ versus L results of Run #19 are shown in Figure 14. In this case, with no fines destruction, there is no reduction of crystal numbers at any size.

The PE concentration in solution is displayed as a function of temperature in Figures 16 through 18. The saturation PE concentration is also given. The difference between the actual and saturation concentrations reveals the supersaturation at any temperature. In all three experiments, the supersaturation decreases rapidly when the temperature reaches 65°C . It then appears to maintain a roughly constant value for the duration of the run. Runs #18 and 20 maintained a slightly higher supersaturation during this period than did Run #19.

The solution concentration and supersaturation is shown as a function of time for all three runs in Figures 19 through 21. The concentration is constant until the solution nucleates. It then decreases as crystal growth occurs. The time of nucleation is determined by the intersection of the straight line through the constant concentration points and the best curve fit through the remaining points.

Figure 13 Cumulative Number Distributions of Run #18.

Figure 14 Cumulative Number Distributions of Run #19.

Figure 15 Cumulative Number Distributions of Run #20.

Figure 16 PE Concentration versus Temperature, Run #18.

Figure 17 PE Concentration versus Temperature, Run #19.

Figure 18 PE Concentration versus Temperature, Run #20.

Figure 19 PE Concentration and Supersaturation vs Time, Run #18.

Figure 20 PE Concentration and Supersaturation vs Time, Run #19.

Figure 21 PE Concentration and Supersaturation vs Time, Run #20.

The measured slurry density, M_t , is shown as a function of time for the three runs in Figure 22. The slurry density of Run #19 increased more rapidly than in Runs #18 and 20 which have similar M_t profiles. The slurry density calculated from solution concentration measurements is presented for the three runs in Figure 23. In this case, the profiles of Runs #19 and 20 are similar while the slurry density of Run #18 increases more slowly with time. The difference between calculated and measured slurry density is shown for all three runs in Figure 24.

The cooling curve used for Run #18 was the same as the one used for all previous batch experiments. However, in Runs #19 and 20 a new curve was used. This can be seen in Figure 25 which gives the temperature versus time history of the three runs. The new cooling curve increased the rate at which Runs #19 and 20 were cooled.

Finally, in Figure 26, a comparison is made of the cumulative number distribution of the first two solid samples taken from all three runs. They are quite consistent in numbers and shape of the distribution. Figure 27 compares the cumulative number distribution of solid samples taken from all three runs after approximately one hour of crystal growth. Runs #18 and 20, both with fines destruction, have similar distributions while Run #19

has a larger number of crystals at any size. This effect was more pronounced at sizes below $200\mu\text{m}$.

Figure 22 Measured Slurry Density versus Time, Runs #18-20.

Figure 23 Calculated Slurry Density versus Time, Runs #18-20.

Figure 24 Calculated-Measured Slurry Density vs Time, Runs #18-20.

Figure 25 Temperature versus Time History of Runs #18-20.

Figure 26 First Two Samples of Runs #18-20.

Figure 27 Samples After One Hour, Runs #18-20.

Growth Rate Experiments

Two growth rate experiments were conducted at 65°C and one at 55°C. In all three, supersaturation and crystal size distributions were monitored with time. The crystal size distribution changes were then analyzed by the method of Misra and White (1971) to determine the average growth rate. The supersaturation corresponding to this growth rate was determined by averaging the supersaturation over the growth rate period.

Results at 65°C

Runs #21 and 22 were conducted at a constant temperature of 65°C. For each run, Figures 28 and 29 demonstrate how the cumulative number distribution changes with time. In both figures the total number of crystals is not constant for the first two samples. The remaining samples do have a constant total number indicating that nucleation is no longer occurring. In Figures 30 and 31 the average growth rate and supersaturation for both runs are shown as a function of time. The initial growth rate, which is very high decreases rapidly as the supersaturation decreases. A comparison of slurry density, M_t , measured and calculated from liquid samples is given in Figures 32 and 33. The correlation between the two is good for Run #22. It is close during the first thirty minutes of Run #21. However after that time period the measured slurry

density decreases while the slurry density calculated from liquid measurements continues to increase. In both runs, the slurry density measured is lower than the calculated slurry density.

Figure 28 Cumulative Number Distributions of Run #21.

Figure 29 Cumulative Number Distributions of Run #22.

Figure 30 Average Growth Rate and Supersaturation vs Time, Run #21.

Figure 31 Average Growth Rate and Supersaturation vs Time, Run #22.

Figure 32 Measured and Calculated Slurry Density vs Time, Run #21.

Figure 33 Measured and Calculated Slurry Density vs Time, Run #22.

Results at 55°C

Run #23 was conducted at a constant temperature of 55°C. The measured cumulative number distribution is shown in Figure 34 and the average growth rate and supersaturation versus time are shown in Figure 35. Again the growth rate decreases with a decrease in supersaturation. The calculated and measured slurry density are shown in Figure 36. Their correlation is good for all but the last data point where the measured slurry density does not increase by the same amount as the calculated slurry density. As seen in the growth rate results at 65°C, the calculated slurry density is higher than what was measured.

Kinetic Parameters

To determine the kinetic parameters k , a , k_g and E_a given in Equation 4, the average growth rate, G , versus supersaturation, S , is plotted on log paper in Figures 37 and 38. The intercept of each line is the value of k_g at that temperature and the slope of each is the value of a . The results of the two runs at 65°C fall on approximately the same line.

Because growth rate experiments were conducted at only two temperatures, the final value of a was taken as the average value measured in the three runs. The values of k

and E_a were determined by averaging the results of Runs #21 and 22 and using the average with the results of Run #23.

Other Results

Other results such as PDI calibration, refractometer calibration and particle size versus removal rate are presented in Appendix A.

Figure 34 Cumulative Number Distributions of Run #23.

Figure 35 Average Growth Rate and Supersaturation vs Time, Run #23.

Figure 36 Measured and Calculated Slurry Density vs Time, Run #23.

Figure 37 Average Growth Rate vs Supersaturation, Runs #21 and 22.

Figure 38 Average Growth Rate vs Supersaturation, Run #23.

DISCUSSION OF RESULTS

Effect of Fines Destruction on the Final CSD: Seeded Batch Experiments

Runs #1-12 were conducted to determine a preliminary estimate of how fines destruction would change the final CSD of a batch crystallized pentaerythritol solution. They also provided operator experience and an opportunity to work out equipment problems that are characteristic of any new system. During their course experimental technique was constantly modified and improved. Thus, the results were used as an initial indication of the feasibility of fines destruction in batch crystallization.

The cumulative number distribution of the runs without fines destruction does not vary considerably as seen previously in Figure 10. Thus, the log average of the five runs is used to calculate the population density distribution shown in Figure 39. Also shown in Figure 39 is the population density distribution calculated from the log average of the CSD of the seven runs that used fines destruction. Although there is a wide variation of CSD in runs with fines destruction the log average is used for comparison purposes. Differences between the two curves can be attributed solely to the implementation of fines destruction.

Figure 39 Population Density Distribution, Log Ave. Runs #1-12.

Table 4 lists a summary of results of Runs #1-12. Theoretically, the runs with a higher fines removal rate should have a greater reduction of small crystal numbers. This is not the case as Run #12 with a fines removal rate of $2.8 \times 10^{-6} \text{ m}^3/\text{s}$ has a greater reduction of small crystals than Runs #8 and 9 which had a fines removal rate of $4.3 \times 10^{-6} \text{ m}^3/\text{s}$. On the other hand, Run #7 with a fines removal rate of only $2.1 \times 10^{-6} \text{ m}^3/\text{s}$ has approximately the same final CSD as Runs #8 and 9. However, because Runs #1-12 were preliminary in nature, the observation that the number of small crystals was reduced is more important than the magnitude of the reduction.

Table 4
Summary of Results Runs #1-12

Run #	M_t kg/m ³	Q_F m ³ /s x10 ⁶	L_F mx10 ⁶	$\bar{L}$ mx10 ⁶
1	220	0	0	290
2	250	0	0	190
3	220	0	0	200
4	240	0	0	230
5	260	0	0	220
6	160	*	*	390
7	180	2.1	310	300
8	220	4.3	640	290
9	200	4.3	640	300
10	240	0	0	270
11	260	0	0	210
12	170	2.8	420	420

* Not Measured.

Effect of Fines Destruction on the Final CSD
Non-Seeded Batch Experiments

The improvement in the final CSD of a "crash-nucleated" batch experiment due to the use of fines destruction was seen in Figure 12. The final cumulative number distribution is constant for the three runs without fines destruction. Runs #14 and 17, which had fines destruction, show a significant reduction in the number of crystals smaller than $300\mu\text{m}$ and an increase in the number of crystals larger than that size.

Because the CSD is constant for the three runs without fines destruction the log average is used to calculate the population density distribution. Figure 40 compares this distribution with the population density distributions calculated for Runs #14 and 17.

Inspection of the cumulative number and population density results reveals that the cumulative number and number density of small crystals was reduced by a greater amount in Run #17 than in Run #14. However, as seen in Table 5, the fines removal rate was almost constant for both. The discrepancy can be explained by the fact that a different coil was used to heat the fines stream in the two runs. As stated in the Results section, Run #17 used a coil for fines dissolving that had a larger surface area and residence time than the coil used for Run #14 and all previous runs. Fluid passing through the coil with the

Figure 40 Population Density Distributions of Runs #13-17.

greater surface area will be heated to a temperature closer to the hot water temperature bath and a larger percentage of the fines will be dissolved. The increased residence time in the coil with the larger surface area will also act to improve dissolution of the fines.

Both runs with fines destruction had a significant increase in the number of crystals larger than $450\mu\text{m}$ as compared to the runs without fines destruction. This improvement in the CSD is also seen in the increased average crystal size as shown in Table 5.

Table 5
Summary of Results Runs #13-17

Run #	M_t kg/m^3	Q_F $\text{m}^3/\text{s} \times 10^6$	L_F $\text{m} \times 10^6$	$\bar{L}$ $\text{m} \times 10^6$
13	200	0	0	260
14	260	3.8	570	380
15	215	0	0	280
16	230	0	0	230
17	210	3.7	550	460

Effect of Fines Destruction:
Transient CSD Changes

Inspection of Figures 13-15 reveals how fines destruction affects the cumulative number distribution throughout a batch crystallization experiment. In Run #19, without fines destruction, Figure 14, the initial crystal size distribution formed by nucleation grows and increases in number the entire batch time period. Contrasted with that, Runs #18 and 20, as seen in Figures 13 and 15, have little increase in crystal numbers after the first sample. After approximately 20 minutes the number of crystals smaller than $100\mu\text{m}$ is reduced. The incorporation of fines destruction in these two runs thus decreases the crystal numbers at smaller sizes.

Population density plots for the three runs, Figures 41-43, demonstrate the effect in a more pronounced manner. Figure 42 shows the population density distribution changes with time for Run #19. Below $100\mu\text{m}$, the population density is fairly constant for all but the first sample. For sizes greater than $100\mu\text{m}$ the population density increases slightly with time. This is more pronounced at the larger sizes indicating size dependency or size dispersion of the growth rate. Regardless of the growth rate mechanism, the population density distribution increases for all sizes greater than $\approx 100\mu\text{m}$.

Figure 41 Population Density Distributions of Run #18.

Figure 42 Population Density Distributions of Run #19.

Figure 43 Population Density Distributions of Run #20.

The population density changes are quite different in Runs #18 and 20. Comparison of Figures 41 and 43 reveals that in both runs, the population density of crystals in the 100-400 μ m range decreases with time. This is not consistent with the changes predicted using the population balance equations presented in the Theory section because in these calculations case, the crystals were all assumed to grow at the same rate.

Figure 44 is a theoretical prediction of population density changes caused by a fines removal rate that destroys crystals below a size L_F at a rate higher than the growth rate. Comparison of Figure 44 with the results of Run #18 and 20 shows that a reasonable agreement exists between the actual and predicted results.

The differences between the CSD of Runs #18 and 20 can be attributed to two things, the fines removal rate was much higher in Run #18 than in Run #20 and a new cooling curve was used for Runs #19 and 20. The new cooling curve is shown in Figure 6. Two changes were made. First, previous observation had shown that crystals did not form in a solution with a PE concentration of 359kg/m³ until the temperature was lowered to approximately 65°C. Therefore, the hour spent cooling the solution to that temperature was eliminated. Second, the solution was cooled at a faster

rate to increase supersaturation and growth rate and to decrease the overall batch time.

Figure 44 Population Changes due to F.D., No Growth of Small Crystals.

The fines removal rate for Run #18 was set at $3.7 \times 10^{-6} \text{ m}^3/\text{s}$. This is 57% higher than the rate of $2.3 \times 10^{-6} \text{ m}^3/\text{s}$ used in Run #20. The increased fines removal rate in combination with a longer batch time allowed the smaller crystals in Run #18 to have a longer exposure time to fines destruction.

Table 6 summarizes the measured slurry density, M_t , the fines removal rates, the fines size, L_F and the average crystal size for the three runs.

Table 6
Summary of Results Runs #18-20

Run #	Q_F $\text{m}^3/\text{s} \times 10^6$	L_F $\text{m} \times 10^6$	$\bar{L}^a$ $\text{m} \times 10^6$	$\bar{L}^b$ $\text{m} \times 10^6$
18	3.7	550	500	300
19	0	0	280	50
20	2.3	350	390	90

a: Calculated using sieve data only.

b: Calculated using both sieve and PDI data.

An estimate of the efficiency of the cooling curve in maintaining a constant supersaturation can be obtained by examining the concentration of PE in solution versus temperature. This was shown for the three runs in Figures 16-18. The saturation concentration is also shown.

As the solution is cooled, the concentration remains constant until the solution nucleates. At that point, it drops rapidly. Further changes are then dictated by crystal growth and cooling rate. It would be expected that in Run #18, which used a slower cooling rate, the concentration would be closer to the supersaturation value than in Runs #19 and 20. However, this is not the case. The concentration at a given temperature in Run #18 is greater than the concentration found in Runs #19 or 20 at the same temperature.

When the concentration is plotted as a function of time as in Figures 19-21 the time at which nucleation occurred can be determined. While the solution is cooling, but before it nucleates, the concentration stays constant. Then, after nucleation, concentration rapidly drops off. The intersection of the constant concentration line with the best curve fit of the remaining points defines the time of nucleation. The effect of the cooling curve used can also be seen in these plots. Run #18 was cooled more slowly than Runs #19 and 20. Because of this, the concentration in Figure 19 does not drop off at the same rate as in Figures 20 and 21.

The nucleation point can be checked by plotting the calculated supersaturation as a function of time, as shown in Figures 19-21. As the solution cools, the

supersaturation increases rapidly. After nucleation, supersaturation declines.

Slurry Density, M_t

Changes in measured slurry density with time for Runs #18-20 are shown in Figure 22. This figure shows a significant difference between Run #19 with no fines destruction and Runs #18 and 20 with fines destruction. Throughout the entire batch period Run #19 had a much higher measured slurry density than the other two runs. The measured slurry densities of Runs #18 and 20 are the same, although it would be expected that the slurry density of Run #18 would not increase as fast as the slurry density of Run #20 because Run #18 was cooled at a slower rate.

A different observation can be made from Figure 23 which shows the slurry density calculated from solution mass fraction measurements. At any given time, both Runs #19 and 20 have a higher calculated slurry density than Run #18 as expected. The amount of time taken for each run to reach a given temperature can be determined from Figure 25. Run #18 required ninety-five minutes to reach 50°C while Runs #19 and 20 required 70 and 65 minutes respectively. If the M_t calculated for all three runs is compared at equivalent temperatures rather than times, the values are 165, 175 and 182 kg/m³, a variation of less than 10%.

Thus, the calculated slurry densities are consistent with each other and vary as expected with changes in cooling curves.

A possible cause of the discrepancies can be found in Figure 24 which compares the difference between the measured and calculated slurry density of all three runs. In all three runs the calculated slurry density is higher than the measured slurry density. Table 7 shows the difference between the two values calculated for each point.

The difference between measured and calculated slurry density could be caused by inadequate circulation in the crystallizer. Larger crystals may not be carried high enough in the annulus to be drawn through the sample port. Also, fouling on the cooling coil will remove PE from the solution and reduce the solution mass fraction while not increasing the slurry density.

There appears to be a constant difference of approximately 30kg/m^3 between the calculated and measured slurry density in Runs #18 and 19. This can be explained by a combination of fouling and crystal size segregation. While Run #18 should have more fouling than Run #19 due to the increased fines cooling load, Run #19 would have more fouling than Run #18 because of the increased cooling rate. Run #18 would also have a larger average crystal size due to

finest destruction. These two effects are apparently equal and thus shows a constant difference in slurry density.

Run #20 has a combination of both finest destruction and faster cooling rate. Thus, the difference between calculated and measured slurry density should be higher. However, it would not be expected that the difference would be three times that seen in Runs #18 and 19. It is possible that the sample port was partially blocked during the course of Run #20. This would cause a decrease in the measured slurry density while not affecting the calculated M_t .

Table 7
Calculated and Measured Slurry Density
Runs #18-20

Time After Nuclea- tion min	Run #18			Run #19			Run #20		
	M_t calc. kg/m ³	M_t meas. kg/m ³	ΔM_t	M_t calc. kg/m ³	M_t meas. kg/m ³	ΔM_t	M_t calc. kg/m ³	M_t meas. kg/m ³	ΔM_t
20	45	35	10	78	65	13	95	35	40
30	64	45	19	100	82	18	117	45	72
40	80	55	25	120	96	24	137	55	82
50	95	64	31	139	110	29	155	64	91
60	110	76	34	158	129	29	173	76	97
70	125	91	34	176	147	29	192	91	101
80	143	112	31	195	164	31	208	112	96
90	166	137	29	-	-	-	-	-	-
100	193	162	31	-	-	-	-	-	-

Growth Rate Experiments

Growth Kinetics

Figures 28, 29 and 34 show that the cumulative number curves are not parallel to each other. It appears that the small crystals grow more slowly, as seen by a small shift at the smaller sizes in the cumulative number curves. The larger crystals grow more rapidly causing a greater shift in the cumulative number curve during the same time period.

The growth rate of PE was calculated by measuring the size change between each sample at cumulative number values of 7.0×10^7 and 1.5×10^8 $\#/m^3$, averaging the two values, and then dividing by the time period. This method should be independent of the cumulative number values used if crystal growth was independent of size. However, as mentioned previously, the growth of PE is not size independent and thus the growth rate calculated will depend on the cumulative number values used. For consistency, the same values were used in the analysis of all three runs.

Growth rate kinetics of PE were calculated as a function of supersaturation expressed on a mass fraction rather than concentration basis. The numbers obtained can then easily be compared with those reported by Creasy et. al. (1974 and 1976). Table 8 presents a summary of values calculated in this study and those reported previously.

Table 8
Comparison of Growth Rate Results

Growth Rate Form: $G = k \Delta x^a \exp(-E_a/RT)$

	a	E_a (kJ/mol)	K (m/s)
This Study	3.3	54	1.2×10^6
Creasy et.al (1976)	2	83	2.4×10^{11}

Growth Rate Form: $G = k (\Delta x/x^*)^a \exp(-E_a/RT)$

	a	E_a (kJ/mol)	K (m/s)
This Study	3.3	90	1.3×10^9
Creasy et.al (1974)	2	125	3.2×10^{12}

Where: x = mass fraction of PE.

x^* = mass fraction of PE at equilibrium.

$\Delta x = x - x^*$

Results of this study do not correlate well with the previously reported data. Several explanations are offered here. In all experimentation Creasy et. al. assumed a

supersaturation exponent of exactly 2. They did observe early time data that indicated a supersaturation exponent with a value greater than two. However, they concluded that its high value was due to seed crystal mending rather than growth. After one to two hours of crystal growth the supersaturation dependence would become two and after that point they reported true crystal growth kinetics could be observed. In this study, seed crystals were not used and thus the mechanism of mending must be discounted. No change in crystal growth mechanism (as indicated by a change in the supersaturation exponent value) was observed. However, experiments were not carried out for the length of time that may have been necessary to observe such changes.

It should be noted that regardless of when the true growth rate kinetics are observed, industrial crystallizers operate at the highest growth rate possible which still produces crystals within specifications. Thus, data presented here would be more applicable for analysis of existing systems.

The activation energy and growth rate constant values calculated in this study were both lower than reported by Creasy et. al. Again, this is probably due to the different time frame used. Also, in this study, the growth rate was measured at only two temperatures which did

not span a wide range. Thus, the two points obtained can only be used for an estimate of the activation energy E_a .

During all three experiments, crystal formation by nucleation occurred along with crystal growth. This can be seen in Figures 28, 29 and 34 as a progressive shifting of the curves to higher cumulative numbers at the smallest crystal sizes. However, after approximately 20 minutes the total number of crystals remained constant and changes in the CSD were only due to crystal growth. Misra and White (1971) presented a method of estimating the nucleation rate from the change in cumulative number with time. Following their procedure the nucleation rate was calculated as a function of supersaturation, s and is shown in Figures 45 and 46. The results at 65 °C, Figure 45, appear to be inconclusive, however a correlation may be possible at 55 °C, Figure 46.

Slurry Density

The correlation between measured and calculated slurry density is good during the first half of Run #21 and for the entire time period of Runs #22 and 23 as expected. Fouling of the cooling coils at constant temperature would be minimal compared to fouling that what would occur in a batch crystallization run.

Figure 45 Nucleation Rate of PE vs Supersaturation, Run #22.

Figure 46 Nucleation Rate of PE vs Supersaturation, Run #23.

CONCLUSIONS

1. The use of fines destruction reduced the number of small crystals and increased the average crystal size, thus improving the crystal size distribution.
2. The measured growth rate of PE is dependent upon the time frame in which the measurements are made. Growth rate kinetics measured immediately after nucleation indicate a high dependence on supersaturation with a supersaturation exponent greater than 2, a growth rate constant equal to $1.3 \times 10^9 \text{ m/s}$ and an activation energy, E_a of 90kJ/mol.
3. Either Pentaerythritol crystal growth rate is size-dependent or the crystals exhibit growth rate dispersion.
4. Slurry density calculated from the concentration changes during a run provides an important check of the measured slurry density and a good indication of fouling in the system.
5. Fines dissolving appears to be a useful technology for improving particle size distribution in a batch crystallizer.

NOMENCLATURE

a	Supersaturation exponent
B°	Nucleation rate, $\#/m^3 \cdot s$
C_{PE}	PE concentration, kg/m^3
C_{PE}^*	Saturation PE concentration, kg/m^3
E_a	Activation energy, kJ/mol
F	Cumulative percentage of crystals smaller than size L , %
G	Linear growth rate, m/s
h	Fines removal frequency, s^{-1}
k	Growth rate pre-exponential constant, m/s
k_g	Growth rate constant, m/s
L	Crystal size, m
L_F	Largest size removed by fines stream, m
M_t	Slurry density per unit of clear liquor, kg/m^3
m_s	Mass of dried crystals, g
m_t	Total mass of a sample, g
n	Population density, $\#/m^4$
N_t	Total number of crystals per unit volume, $\#/m^3$
n_s	Population density of seed crystals, $\#/m^4$
n°	Nuclei population density, $\#/m^4$

Q_F	Fines removal rate, m^3/s
R	Gas Constant, $kJ/mol \text{ } ^\circ K$
s	Supersaturation, kg/m^3
S	Supersaturation, C_{PE}/C_{PE}^*
t	Time, s
T	Temperature, $^\circ C$
v_t	Total volume of a sample, ml
v_l	Liquid volume of a sample, ml
V	Volume of the crystallizer, m^3
x_{PE}	PE mass fraction
x_{PE}^*	PE mass fraction at saturation
Δx_{PE}	Supersaturation
$\Delta x_{PE}/x_{PE}^*$	Supersaturation
α	Number of turnovers in time Δt
ϕ	Fines destruction function
θ'	Non-dimensional temperature
z	Non-dimensional time

APPENDIX A

Calibration of the PDI Particle Counter

Figure 47 shows the results of the calibration of the PDI particle counter. The readings from the various sized calibration particles fall on a straight line. The 44.6 μ m particles were then used for the final calibration of the particle counter because these results were linear throughout the entire channel range.

The results of the a balance check on the PDI are shown in Table 9. For each check, the size of the particles used, the number of count readings taken and their average are shown along with the calculated and known slurry density. The difference between the actual and calculated slurry density varies between $\pm 40\%$ of the actual M_t . This corresponds to only a $\pm 3\%$ error in particle diameter measurement.

Figure 47 Results of the PDI Particle Counter Calibration.

Table 9
Results of Mass Balance Check of PDI

PARTICLE SIZE ($\mu\text{m} \times 10^6$)	M_t ACTUAL (kg/m^3)	M_t CALC. (kg/m^3)	% DIFF	# OF COUNTS	RC_{ave}	LT SETTING
96	0.222	0.211	- 5	9	1116	20
		0.227	2	7	1184	20
		0.273	23	6	1488	10
		0.250	13	5	1365	10
96	0.192	0.212	10	4	2909	5
		0.274	43	2	7218	5
		0.269	40	8	1810	10
		0.264	38	6	1727	10
		0.170	-12	5	1024	20
96	0.196	0.111	-43	5	1792	1
		0.264	35	5	2272	5
		0.262	34	6	1594	10
		0.253	29	4	1586	10
96	0.0833	0.106	27	8	880	5
		0.118	41	8	894	5
		0.100	20	11	587	10
		0.091	9	8	552	10
48	0.0149	0.0116	-22	8	1392	5
		0.0122	-18	7	1526	5
		0.0122	-18	7	1396	10
		0.0115	-23	6	1652	1
64	0.0223	0.0179	-20	10	1506	5
		0.0178	-20	5	1615	5
		0.0195	-13	7	1742	5
		0.0189	-15	7	1732	5
96	0.0231	0.0311	35	12	244	5
		0.0210	-9	12	124	20
	0.0547	0.0540	-1	7	286	20
		0.0615	12	5	318	20
		0.0747	36	8	428	10

Particle Size versus Removal Rate

In Figure 48 the size of particle removed versus the fines removal rate is shown. The removal rate is normalized to the area of the fines trap which was $2.5 \times 10^{-4} \text{m}^2$. Also shown is the maximum particle size removed for a given removal rate as predicted by Stokes Law. The correlation between the measured and predicted results is poor. The actual size removed is much greater than predicted.

Refractometer Calibration

The results of the refractometer are shown in Figure 49. The measured n_d is linear with changes in mass fraction of the solution. The line does not pass through zero mass fraction when the refractive index is 1.333 (the refractive index of pure water). This is due to a shift in the refractometer itself, not an inaccuracy in the results. Thus, this calibration curve is applicable only the refractometer on which it was obtained. The results are also tabulated in Table 10.

o

Figure 48 Particle Size Removed versus Fines Removal Rate.

Figure 49 Results of the Refractometer Calibration.

TABLE 10

Results of the Refractometer Calibration

MASS WATER (g)	MASS PE (g)	X _{PE} (mass fraction)	n _D , 30 °C
47.92	0.4171	0.0086	1.3336
24.30	0.3225	0.0131	1.3343
24.92	0.4728	0.0186	1.3350
49.37	1.1025	0.0226	1.3354
47.68	1.5311	0.0311	1.3367
50.02	1.7325	0.0339	1.3370
50.34	2.0547	0.0392	1.3380
23.99	1.1184	0.0445	1.3385

APPENDIX B

Data

Data from Runs #1-23 is given in Tables 11-32.

Table 11
Sieve Data of Runs #1-4

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Run #1	Run #2	Run #3	Run #4
5	1091	1000	0.72	—	0.13	0.11
6	917	841	6.2	0.45	4.2	4.0
7	771	707	2.3	4.2	1.3	2.2
8	649	595	13.4	3.8	2.6	3.4
9	545	500	16.2	5.9	8.8	13.9
10	458	420	19.0	16.3	23.2	30.0
11	386	354	7.8	15.7	16.6	13.3
12	324	297	6.0	11.2	12.8	6.9
13	273	250	4.1	7.7	5.8	4.2
14	229	210	2.8	6.7	3.2	2.6
15	193	177	1.0	3.9	1.4	2.1
16	162	149	1.3	3.3	1.7	2.6
17	136	125	0.4	2.1	1.4	1.8
18	115	105	0.1	0.56	0.53	0.56
19	96	88	—	0.54	0.62	
20	81	74	—	0.33	0.26	

Table 12
Sieve Data of Runs #5-8

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Run #5	Run #6	Run #7	Run #8
5	1091	1000	0.07	2.8	0.05	0.09
6	917	841	0.33	2.6	0.39	0.83
7	771	707	6.0	3.2	0.71	2.8
8	649	595	1.3	15.2	4.1	2.4
9	545	500	3.0	14.0	14.6	5.1
10	458	420	15.0	11.4	18.1	22.6
11	386	354	20.0	3.9	8.1	18.6
12	324	297	16.2	1.9	7.9	10.4
13	273	250	10.8	0.66	4.2	3.2
14	229	210	7.6	0.28	1.8	2.0
15	193	177	2.8	0.12	0.71	0.74
16	162	149	3.8	0.14	0.49	0.91
17	136	125	1.9	0.11	0.30	0.39
18	115	105	0.38	0.06	0.10	0.08
19	96	88	0.34	—	—	0.06
20	81	74	—	—	—	—

Table 13
Sieve Data of Runs #9-12

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Run #9	Run #10	Run #11	Run #12
5	1091	1000	0.60	2.6	0.72	3.0
6	917	841	0.24	0.55	8.8	9.9
7	771	707	0.41	1.3	1.8	1.5
8	649	595	7.1	10.9	5.4	9.1
9	545	500	12.7	14.4	12.3	14.2
10	458	420	15.4	20.6	17.1	11.8
11	386	354	7.1	11.9	9.5	5.8
12	324	297	4.8	8.6	8.9	3.4
13	273	250	2.3	6.3	7.3	1.2
14	229	210	1.2	3.9	5.6	0.42
15	193	177	0.52	1.7	3.3	0.09
16	162	149	0.46	1.3	3.8	-
17	136	125	0.23	0.53	2.2	-
18	115	105	0.07	0.09	0.46	-
19	96	88	0.05	0.09	0.41	-
20	81	74	-	-	-	-

Table 14
Sieve Data of Runs #13-15

Screen	$\bar{L}$ μm	L μm	Mass of crystals m_s reporting to each sieve		
			Run #13	Run #14	Run #15
5	1091	1000	1.57	0.48	—
6	917	841	0.25	1.36	—
7	771	707	2.69	9.91	0.30
8	649	595	8.27	27.06	3.03
9	545	500	10.73	20.00	6.59
10	458	420	13.14	17.54	15.75
11	386	354	9.56	7.16	12.20
12	324	297	10.06	4.83	8.44
13	273	250	7.69	2.27	4.69
14	229	210	5.76	1.23	3.09
15	193	177	2.93	0.49	1.38
16	162	149	2.31	0.46	1.50
17	136	125	1.26	0.23	0.81
18	115	105	0.38	0.07	0.29
19	96	88	0.27	0.05	0.20
20	81	74	0.07	—	—

Table 15
Sieve Data of Runs #16 and 17

Screen #	$\bar{L}$ μm	L μm	Mass crystals on screen i	
			Run #16	Run #17
5	1091	1000	—	0.24
6	917	841	—	0.91
7	771	707	1.73	6.06
8	649	595	3.86	14.83
9	545	500	6.93	8.87
10	458	420	11.22	2.76
11	386	354	10.41	1.17
12	324	297	12.92	0.71
13	273	250	10.22	0.34
14	229	210	9.04	0.18
15	193	177	6.36	0.07
16	162	149	5.82	0.07
17	136	125	3.61	—
18	115	105	1.05	—
19	96	88	0.64	—
20	81	74	0.15	—

Table 16
Sieve Data of Run #18

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#1	#2	#3	#4
5	1091	1000	0	0	0	0
6	917	841	0	0.07	0.06	0.10
7	771	707	0	0.04	0.04	0.08
8	649	595	0	0.06	0.05	0.21
9	545	500	0	0.11	0.08	0.46
10	458	420	0	0.26	0.22	0.93
11	386	354	0.03	0.38	0.23	0.78
12	324	297	0.01	0.47	0.24	0.64
13	273	250	0.03	0.37	0.17	0.38
14	229	210	0.03	0.26	0.11	0.24
15	193	177	0.03	0.13	0.06	0.12
16	162	149	0.03	0.15	0.06	0.12

Table 17
Sieve Data of Run #18

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#5	#6	#7	#8
5	1091	1000	0.15	0	0.10	0
6	917	841	0.07	0	0.21	0.04
7	771	707	0.18	0.09	1.31	0.92
8	649	595	0.62	0.79	2.85	5.15
9	545	500	1.17	1.76	1.49	2.36
10	458	420	1.45	1.31	0.68	0.86
11	386	354	0.79	0.41	0.19	0.23
12	324	297	0.50	0.20	0.11	0.12
13	273	250	0.25	0.11	0.05	0.06
14	229	210	0.16	0.05	0.03	0.02
15	193	177	0.08	0.03	0.01	0.01
16	162	149	0.11	0.02	0.01	0.01

Table 18
Sieve Data of Run #19

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#1	#2	#3	#4
5	1091	1000	0	0.07	0.10	0.15
6	917	841	0.01	0.01	0.01	0.01
7	771	707	0.01	0.01	0.03	0.04
8	649	595	0.01	0.01	0.13	0.30
9	545	500	0.01	0.07	0.39	0.72
10	458	420	0.03	0.27	0.94	0.98
11	386	354	0.03	0.64	0.52	0.52
12	324	297	0.16	0.59	0.45	0.46
13	273	250	0.58	0.29	0.29	0.30
14	229	210	0.31	0.23	0.20	0.22
15	193	177	0.15	0.14	0.11	0.13
16	162	149	0.15	0.15	0.12	0.12

Table 19
Sieve Data of Run #19

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#5	#6		
5	1091	1000	0.19	0.25		
6	917	841	0.03	0.04		
7	771	707	0.12	0.24		
8	649	595	0.66	0.91		
9	545	500	1.20	1.16		
10	458	420	0.96	0.82		
11	386	354	0.58	0.53		
12	324	297	0.52	0.48		
13	273	250	0.33	0.23		
14	229	210	0.24	0.25		
15	193	177	0.14	0.16		
16	162	149	0.15	0.17		

Table 20
Sieve Data of Run #20

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#1	#2	#3	#4
5	1091	1000	0.01	0.05	0.05	0.04
6	917	841	0	0	0	0.01
7	771	707	0.01	0.01	0.02	0.04
8	649	595	0.01	0.02	0.05	0.11
9	545	500	0.01	0.04	0.13	0.19
10	458	420	0.04	0.12	0.25	0.30
11	386	354	0.10	0.17	0.24	0.25
12	324	297	0.24	0.25	0.31	0.26
13	273	250	0.27	0.19	0.24	0.15
14	229	210	0.28	0.18	0.18	0.10
15	193	177	0.18	0.11	0.10	0.04
16	162	149	0.20	0.13	0.11	0.04

Table 21
Sieve Data of Run #20

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#5	#6	#7	
5	1091	1000	0.04	0.20	0.28	
6	917	841	0.02	0.05	0.12	
7	771	707	0.07	0.30	0.66	
8	649	595	0.23	0.69	1.18	
9	545	500	0.37	0.82	1.04	
10	458	420	0.51	0.86	0.92	
11	386	354	0.35	0.47	0.39	
12	324	297	0.32	0.32	0.23	
13	273	250	0.13	0.13	0.08	
14	229	210	0.09	0.07	0.04	
15	193	177	0.04	0.03	0.02	
16	162	149	0.04	0.03	0.03	

Table 22
Sieve Data of Run #21

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#1	#2	#3	#4
5	1091	1000	0	0	0	0
6	917	841	0	0	0	0
7	771	707	0	0.07	0.11	0.09
8	649	595	0	0.19	0.28	0.31
9	545	500	0.09	0.55	0.80	0.71
10	458	420	0.42	0.95	0.80	0.67
11	386	354	0.36	0.61	0.55	0.47
12	324	297	0.36	0.67	0.71	0.49
13	273	250	0.24	0.46	0.47	0.36
14	229	210	0.21	0.29	0.30	0.25
15	193	177	0.13	0.14	0.15	0.11
16	162	149	0.15	0.16	0.17	0.12

Table 23
Sieve Data of Run #22

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#1	#2	#3	#4
5	1091	1000	0	0	0	0
6	917	841	0	0	0	0
7	771	707	0	0	0	0.06
8	649	595	0.01	0.03	0.09	0.18
9	545	500	0	0.05	0.30	0.53
10	458	420	0.01	0.23	0.59	0.72
11	386	354	0.01	0.42	0.50	0.56
12	324	297	0.17	0.43	0.50	0.57
13	273	250	0.18	0.32	0.39	0.39
14	229	210	0.15	0.27	0.30	0.30
15	193	177	0.07	0.17	0.17	0.15
16	162	149	0.10	0.19	0.18	0.17

Table 24
Sieve Data of Run #22

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#5	#6	#7	
5	1091	1000	0	0	0	
6	917	841	0	0	0	
7	771	707	0.10	0.10	0.08	
8	649	595	0.20	0.32	0.30	
9	545	500	0.60	0.75	0.64	
10	458	420	0.72	0.93	0.78	
11	386	354	0.59	0.72	0.63	
12	324	297	0.57	0.75	0.59	
13	273	250	0.37	0.44	0.40	
14	229	210	0.26	0.32	0.28	
15	193	177	0.13	0.16	0.16	
16	162	149	0.16	0.18	0.20	

Table 25
Sieve Data of Run #23

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#1	#2	#3	#4
5	1091	1000	0	0	0	0.05
6	917	841	0	0	0.05	0.06
7	771	707	0	0.03	0.18	0.33
8	649	595	0.04	0.18	0.52	0.53
9	545	500	0.09	0.23	0.37	0.28
10	458	420	0.20	0.18	0.26	0.22
11	386	354	0.14	0.09	0.17	0.17
12	324	297	0.11	0.09	0.16	0.22
13	273	250	0.05	0.06	0.16	0.20
14	229	210	0.05	0.07	0.14	0.14
15	193	177	0.02	0.06	0.08	0.07
16	162	149	0.03	0.06	0.08	0.08

Table 26
Sieve Data of Run #23

Screen #	$\bar{L}$ μm	L μm	Mass of crystals reporting to each sieve, g			
			Sample			
			#5	#6		
5	1091	1000	0.04	0.08		
6	917	841	0.11	0.20		
7	771	707	0.37	0.57		
8	649	595	0.45	0.42		
9	545	500	0.22	0.26		
10	458	420	0.21	0.29		
11	386	354	0.20	0.30		
12	324	297	0.25	0.33		
13	273	250	0.18	0.24		
14	229	210	0.13	0.19		
15	193	177	0.09	0.12		
16	162	149	0.10	0.15		

Table 27
Summary of Samples, Run #18

Time, min from start	Time, min from nucleation	x _{pE}	Sample #	M _t (kg/m ³)
3	—	0.272		
31	—	0.270		
36	—	0.272		
42	6		1	8
48	12		2	25
57	21	0.241		
60	24		3	39
68	31	0.232		
70	34		4	48
77	41	0.225		
88	52		5	64
90	54	0.212		
101	65	0.205		
110	74	0.191		
112	76		6	123
118	82	0.185		
128	92	0.167		
130	94		7	155
138	102		8	130
140	104	0.136		

Table 28
Summary of Samples, Run #19

Time, min from start	Time, min from nucleation	x _{pE}	Sample #	M _t (kg/m ³)
0	-	0.249		
3	-	0.257		
4	-	0.252		
7	-	0.262		
12	-	0.262		
14	1		1	11
17	4	0.246		
18	5	0.246		
21	8		2	34
22	9	0.239		
27	14	0.228	3	51
37	24	0.214	4	70
47	34	0.203	5	86
57	44	0.194	6	97
67	54	0.177	7	120
77	64	0.164	8	133
87	74	0.142	9	155
92	79	0.134		
94	81	0.120		

Table 29
Summary of Samples, Run #20

Time, min from start	Time, min from nucleation	x _{pE}	Sample #	M _t (kg/m ³)
0	—	0.266		
2	—	0.268		
27	—	0.270		
30	0	0.271		
31	1		1	11
34	4		2	22
35	5	0.237		
39	9		3	30
40	10	0.231		
45	15	0.221		
49	19		4	36
55	25	0.207		
59	29		5	44
60	30	0.202		
65	35	0.190		
74	45	0.183		
84	54		6	71
85	55	0.173		
90	60	0.165		
96	66	0.155		
99	69		7	89
100	70	0.143		

Table 30
Summary of Samples, Run #21

Time, min from start	Time, min from nucleation	x _{pE}	Sample #	M _t (kg/m ³)
0	0	-		
6	6		1	25
8	8	0.259		
16	16		2	46
20	20	0.227		
26	26	0.228		
29	29		3	61
33	25	0.231		
39	39		4	65
41	41	0.223		
44	44	0.230		
52	52	0.227	5	60
87	87		6	44
89	89	0.213		
114	114		7	70
122	122	0.211		

Table 31
Summary of Samples, Run #22

Time, min from start	Time, min from nucleation	x_{PE}	Sample #	M_t (kg/m ³)
0	—	0.263		
13	—	0.266		
20	—	0.269		
22	2		1	2
24	4	0.264		
28	8		2	19
33	13	0.244		
41	21	0.240		
48	28		3	44
56	36	0.232		
64	44	0.228		
72	52		4	62
75	55	0.228		
150	130	0.220		
158	138		5	69
289	269		6	76
294	274	0.215		
322	323	0.213		
1508	1489	0.204	7	90

Table 32
Summary of Samples, Run #23

Time, min from start	Time, min from nucleation	x _{pE}	Sample #	M _t (kg/m ³)
0	—	0.219		
8	—	0.220		
12	—	0.223		
14	—	0.219		
16	—	0.223		
20	—	0.216		
22	—	0.222		
27	4	0.214		
28	5		1	8
32	9	0.208	2	16
37	14	0.198	3	26
42	19	0.196		
47	24		4	40
52	29	0.188		
67	44		5	57
72	49	0.172		
102	79	0.173		
127	104		6	71
132	109	0.167		

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