

Effects of Temperature and Cooling Modes on Yield, Purity and Particle Size Distribution of Dihydroxystearic Acid Crystals

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Abstract

An investigation into the effects of temperature and two different cooling modes (i.e. controlled and natural) on the solvent crystallization of dihydroxystearic acid (DHSA) was carried out. The effects of operating temperature and the time on the crystal size distribution (CSD), purity and yield of crystallized DHSA were studied. The crystal purity and average crystal particle size increased with temperature, but the crystal yield decreased as the temperature increased. The controlled cooling crystallization process initially resulted in better crystal properties compared to natural cooling crystallization. However, towards the end of the crystallization process, only marginal differences in terms of crystal properties were observed.

Keywords: Crystallization; agglomeration; purification; dihydroxystearic acid; crystal size distribution

1. Introduction

In today's world, natural ingredient derived from vegetable oil are widely used within the personal care segment. The personal care industry has shown great interests in hydroxyl fatty acids, which are useful intermediates in the synthesis of fine chemical products (Awang et al, 2001; Ismail et al, 2006). Palm based dihydroxystearic acid (DHSA) is one of the plant based hydroxyl fatty acids which can be produced from oleic acid via epoxidation with formic acid followed by hydrolysis of the epoxide (Awang et al, 1998; Koay et al, 2006) The presence of hydroxyl and carboxyl groups in DHSA provided various reaction sites for the preparation of many useful derivatives. Studies have shown that DHSA is suitable as thickener, gelling agent, binding agent, mechanical properties booster and pigment dispersion enhancer in the formulation of decorative cosmetics (Awang et al, 2001; Ismail et al, 2006). The crude waxy DHSA can be purified by employing solvent crystallization as the purification method in order to remove the imbedded impurities, such as octanoic and decanoic acids.

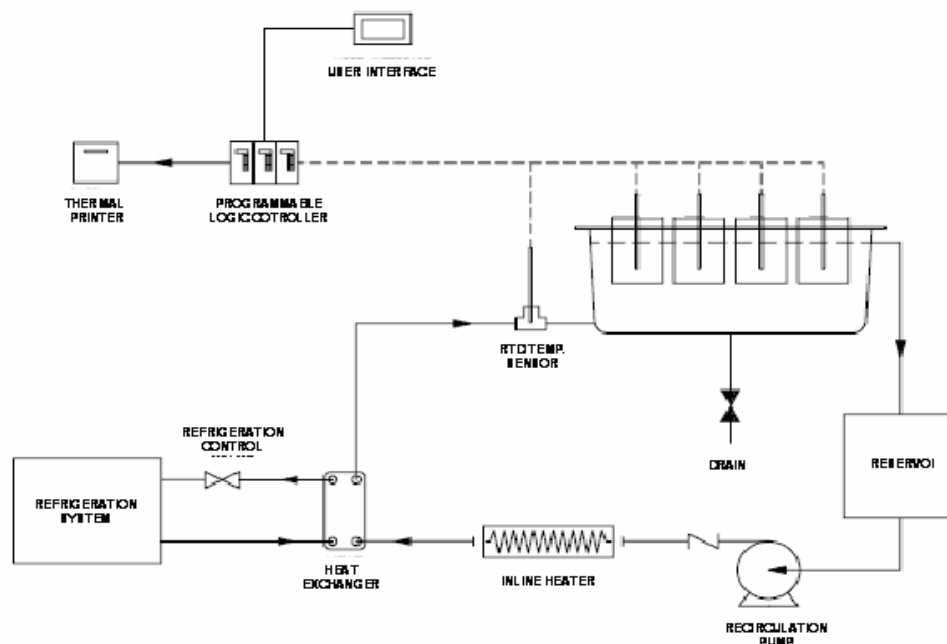
In commercial crystallization, yield and purity are not the only important aspect but also the crystal size distribution (CSD). Industrial crystallization demands for narrow range of CSD and regularity which result in good storage and transportation properties, free flowing nature and pleasant appearance (Timms, 1985). The crystal properties are affected by the crystallization temperature and the initial cooling rate. Controlled cooling crystallization demands very low supersaturation rate and hence very low cooling rate in the early stage of crystallization. Natural cooling crystallization is the simplest with no temperature control, resulting in very high initial cooling rate when the temperature driving force (temperature gradient) is the greatest.

The objectives of this work are to investigate the effect of (i) crystallization temperature, and (ii) initial cooling rate on yield, purity and CSD of the DHSA crystals. The information obtained will be useful for process control of the crystallization to produce crystals of desired properties.

2. Materials and Methods

2.1. Equipment Operation

The investigation into controlled cooling crystallization was carried out using a fabricated crystallizer, which can take up to 12 samples at any one time. The process flow diagram is shown in Figure 1. The temperature of the tank is controlled by balancing between pulse heating and cooling. The heating achieved via an in-line heater and the cooling is achieved via a chiller. The desired cooling rate and crystallization temperature can be activated through a programmable logical controller (PLC). The non-control cooling (natural cooling) crystallization was performed in a conditioned room with an ambient temperature of 24°C.

Figure 1: Process flow diagram of the fabricated controlled cooling crystallizer.

2.2. Experimental Procedures

Twelve beakers with 250g of crude DHSAs each were melted in an oven to a temperature around 80°C for 24 hours to ensure complete melting and the destruction of all crystal memories. The molted DHSAs was then mixed with ethanol at 1:1 w/v ratio, where the solution temperature was found to be around 65°C. Before the samples were placed into the chamber, the crystallizer was preheated to the same temperature (65°C) to ensure that there was no excess heat applied to the solutions which might contribute to solvent evaporation. The cooling rate was fixed at 0.6°Cmin⁻¹. The temperature-time profiles were recorded every 5 minutes. The crystallization process was carried out for 12 hours. The crystals obtained were then segregated from the mother liquor through a vacuum filtration system. The filter media was of nylon fabric with 10µm pore diameter. The crystals were then transferred into petri dishes and dried in an oven at 50°C for 48 hours. For natural cooling crystallization, the 12 samples were placed in a conditioned room with an ambient temperature of 24°C for 12 hours. The time-temperature profile was obtained by recording the temperature at 5 minutes interval for the first three hours and 30 minutes interval after that till the crystallization process ended. All experiments were carried out in triplicates and repeated twice to ensure consistency and reproducibility.

2.3. Materials and Analytical Methods

The product yield is determined by dividing the amount of product formed with the amount of raw material being used, in percentage value. The Gas chromatography (GC) analysis was carried out using a Hewlett-Packard HP-6860A Plus gas chromatograph (Palo Alto, CA). The DHSAs samples had to undergo silylation process before being injected into the GC equipment. The silylation process was carried out by preparing the trimethylsilyl (TMS) derivatives of DHSAs where 0.01g of DHSAs was weighted into a vial followed with the insertion of 2 ml of N, Ndimethylformamide (DMF) and 1ml of Bis(trimethylsilyl)trifluoroacetamide (BTSFA). The vial was then vortexed for 30 seconds in order for the content to achieve homogeneous mixing before being incubated at 60°C for 30 minutes. The derivatives were allowed to cool down for a few minutes. About 1.5ml of the derivatives was then transferred into a 2 ml clear wide opening crimp vial laced with a very small amount of sodium sulphate anhydrous. The vial was sealed off and injection followed. The derivatives concoction was

separated on a non-polar column, HP-5 (Hewlett-Packard, 30 m × 0.25 mm × 0.25 μm) with helium as the carrier gas.

The oven was programmed to hold at 150°C for one minute, followed by ramping from 150 to 290°C at a rate of 10°C per minute. The final temperature was held at 290°C for 30 minutes. The injector and flame-ionization detector were set at 300°C.

2.4. Crystal Size Distribution Analysis

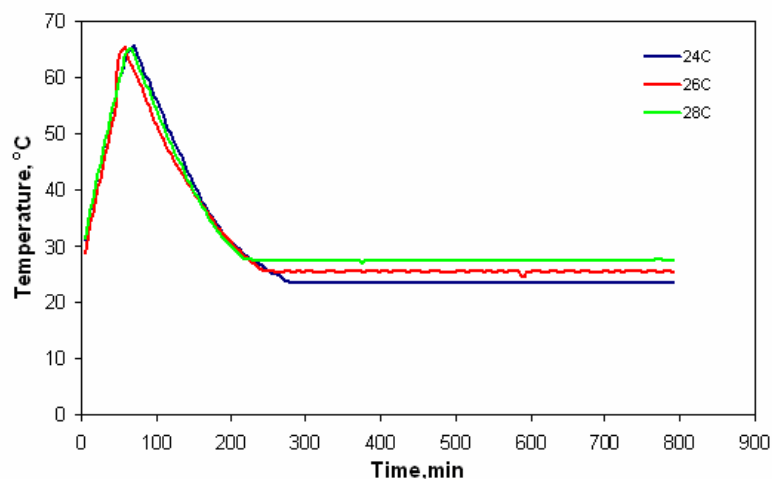
The crystal size distribution (CSD) analysis was carried out by determining the wet dispersion laser diffraction measurements using Malvern Instruments Mastersizer 2000 and Hydro 2000S particle size analyzer (United Kingdom). The equipment was set to process the particle size ranging from 0.020 to 2000.000 μm. The Mie-Scattering analysis model was chosen for the measurement of the diffraction pattern. The principal was based on simultaneous multi angle detection of scattered light where the scattering behavior was strongly dependent on the particle size. In this analysis, the reflective index (RI) of the particle, DHSA, was 1.520 while the RI of the dispersant, water, was 1.330. The Mastersizer 2000's operating procedures were set to record the background measurement for 20 seconds followed by sample measurement for 20 seconds. A small amount of DHSA crystal samples were then inserted into the designated vessel containing water, where they were introduced into the dispersion module, until an adequate obscuration level was obtained and the laser obscuration was stable ($\pm 0.2\%$). The ideal obscuration level ranged from 10.0 to 20.0. A total of three measurement cycles were carried out for each sample and the average value was taken as the final result. The crystal particles' specific surface area, surface weighted and volume weighted mean diameters were determined along with the d(0.1)-, d(0.5)- and d(0.9)-cumulative undersize.

3. Results and Discussion

3.1. Effects of Temperature on Controlled Crystallization of DHSA

For controlled cooling, the samples in the crystallizer were cooled from 65°C to three different temperatures, i.e. 24, 26 and 28°C, respectively, as shown in Figure 2. The crystallization temperature was achieved within two hours of cooling. Sufficient amount of crystals needed for chemical and physical analysis were obtained after 4 to 6 hours from the initiation of the crystallization process. The cooling profiles were found to have similar patterns for all temperatures.

Figure 2: Comparison on time-temperature profile for three crystallization temperatures



The percentage of crystals deposited from the solution versus the solute weight is presented in Figure 3. As expected, the crystal yields increased with time. At the end of the crystallization process, the yields are 35.8, 28.8 and 7.3% for temperature of 24, 26 and 28°C, respectively. Crystal yield increased remarkably as temperature decreased. For an increment of 2°C, the first sampling time was delayed for a least an hour as the growth of DHSA crystals were lower and slower at higher temperature.

Figure 4 shows the average crystal size versus time, measured according to volume weighted mean diameter. As temperature increased, average crystal size increased. At the early stage of crystallization, the crystals attracted with each other, forming large crystals. As time elapsed, individual crystals developed. Consequently, average crystal size remained approximately constant till the end of the crystallization process. Obvious fluctuation occurred for crystallization at 28°C because of low crystal yield. Only from the 11th hour onwards that more crystals were formed and thus segregating among themselves into individual crystals and remained almost constant after that.

Figure 3: Comparison of DHSA yield for three crystallization temperatures.

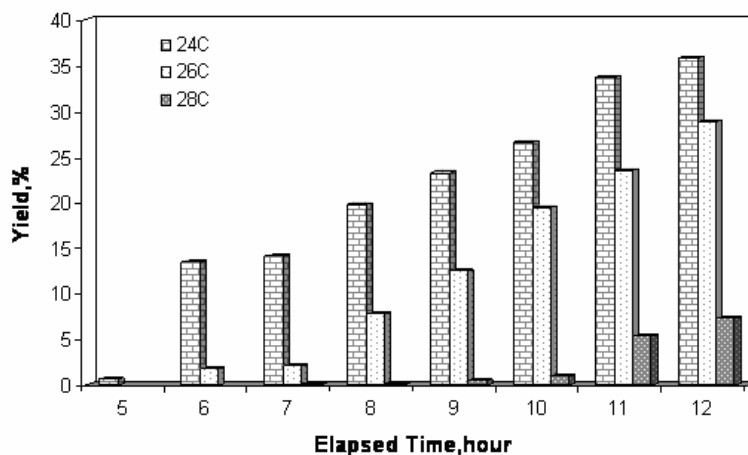
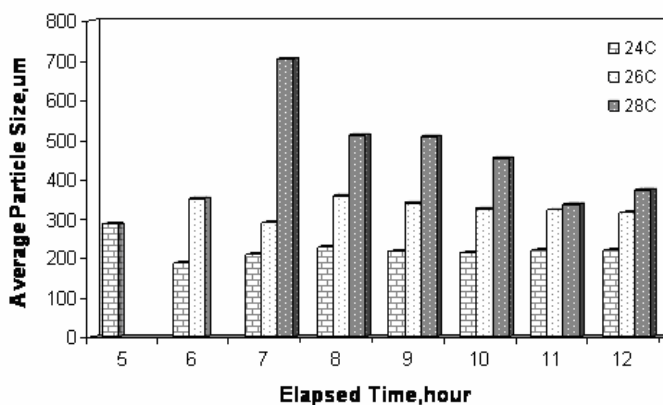


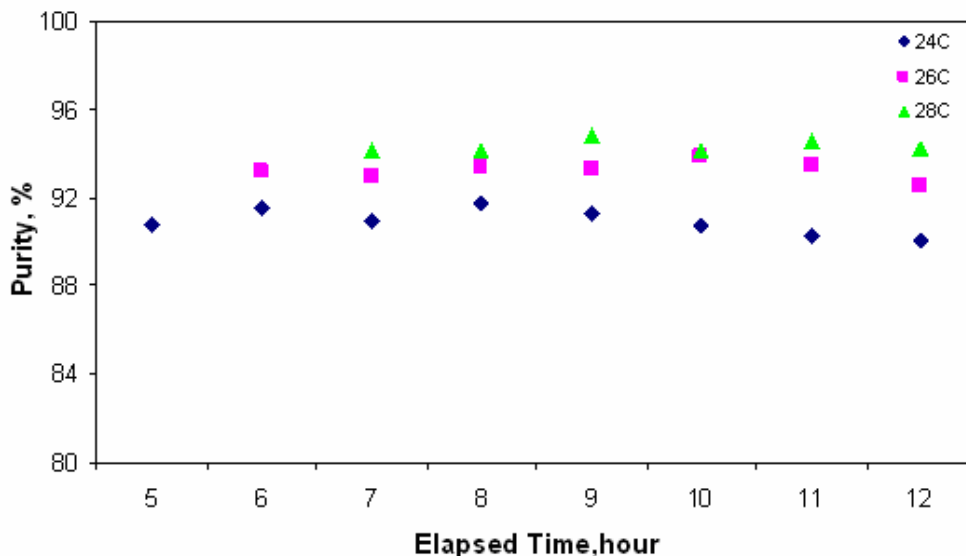
Figure 4: Comparison of average crystal size for three crystallization temperatures.



However, higher crystallization temperature produced purer DHSA crystals, as shown in Figure 5. Nevertheless, the increase of purity over the crystallization time was relatively small, 90.1 to 91.7, 92.5 to 93.9 and 94.1 to 94.7% for temperatures of 24, 26 and 28°C, respectively. Earlier, it was established that the crystallization temperature of 24°C yielded crystals of lower average particle size. Crystals with smaller particle size has higher probability of entrapping mother liquor (Saito et al,

2000), thus compromising the overall product purity, which was what exactly happening as the temperature decreased from 28 to 24°C.

Figure 5: Comparison of crystal purity for three crystallization temperatures.



3.2. Controlled Cooling Crystallization versus Natural Cooling Crystallization

To investigate the effect of initial cooling rate on the crystal properties, the crystallization temperature of 24°C was selected. Figure 6 shows the temperature-time profile for the natural cooling and the controlled cooling modes. The cooling rate of the natural cooling was much faster than the controlled cooling, thus resulting in steeper temperature reduction. After the 200th minutes, the ambient temperature for both cooling conditions converged (Figure 6).

Figure 6: Comparison of temperature-time profile for two cooling modes.

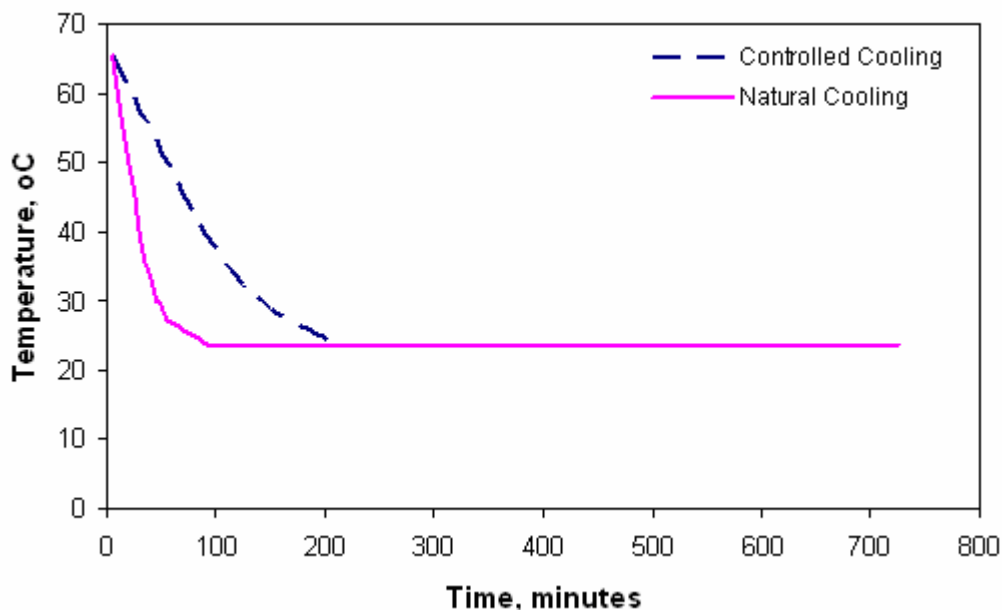


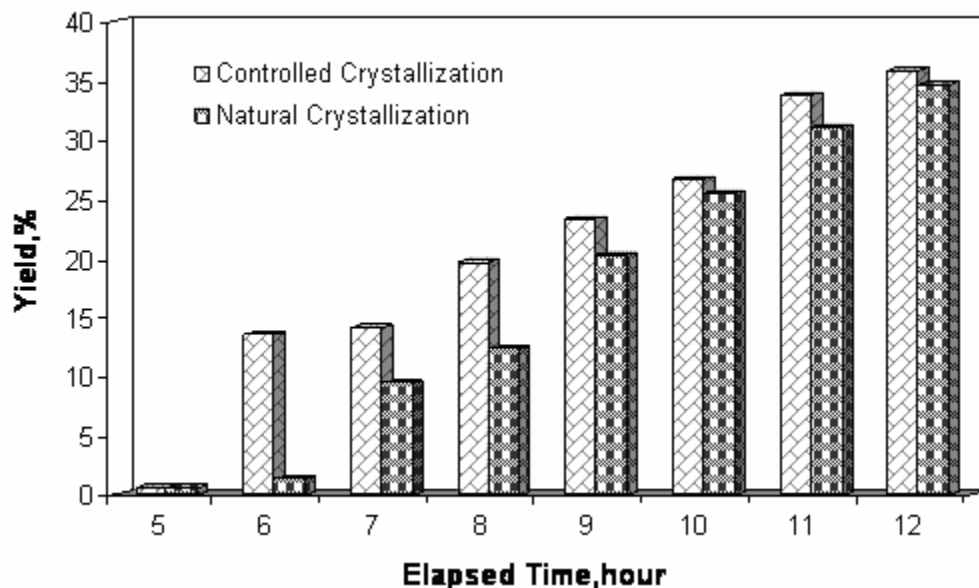
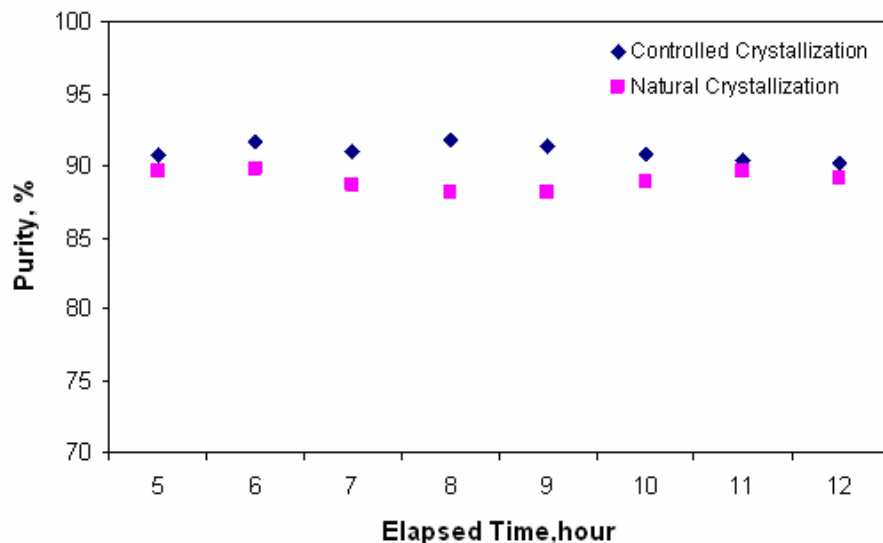
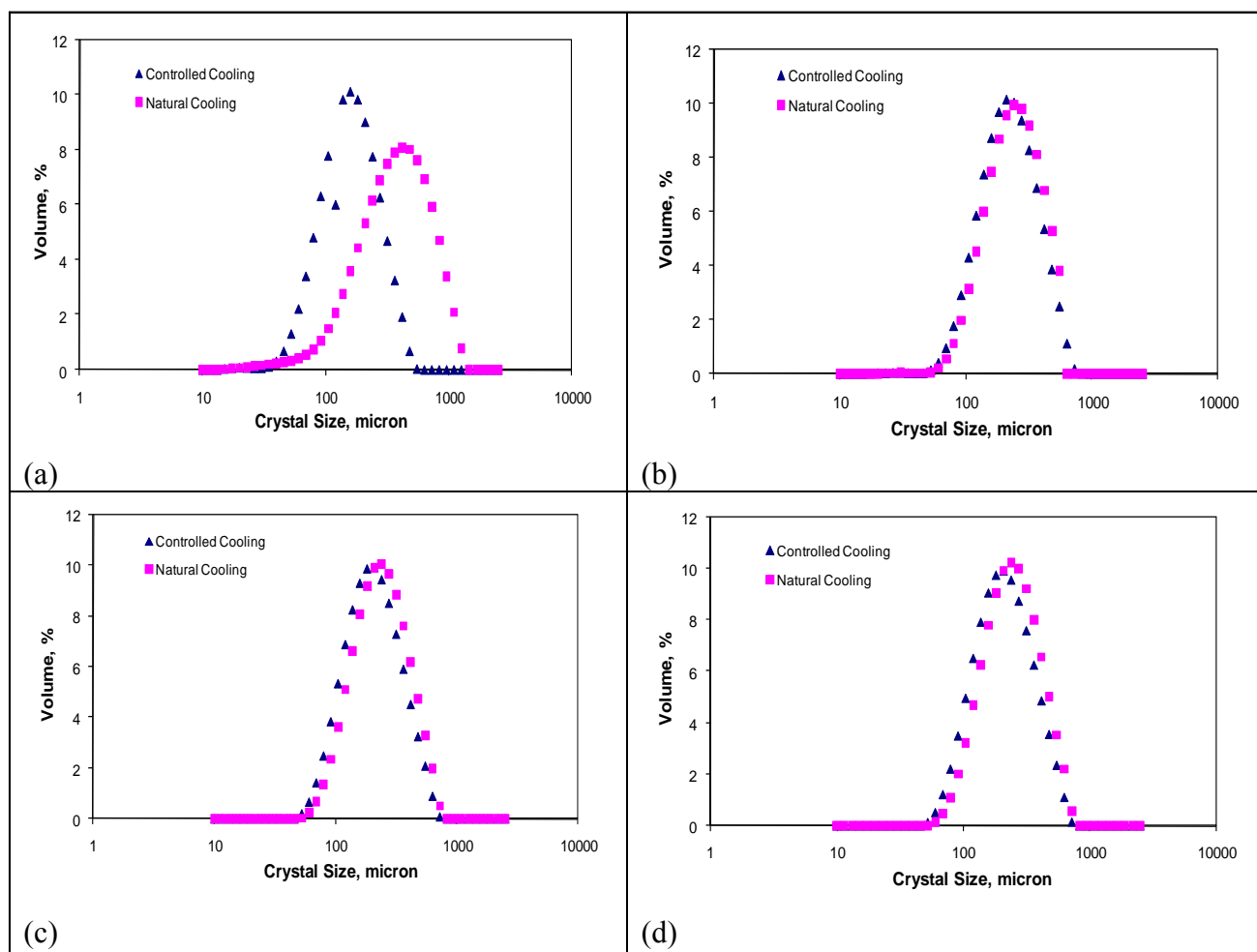
Figure 7: Comparison of yield for two cooling conditions.

Figure 7 shows the yield from controlled and natural cooling crystallization. At the initial stage, very little crystals were formed for both cooling modes. The yield for the controlled cooling increased substantially after 6 hours. There was initially a big difference in yields between the controlled and cooling modes. However, as the crystallization proceeded, the yields for both cooling modes were almost the same at the end of the crystallization process. The purity of the crystals as shown in Fig. 8 demonstrated only a small difference within the 12-hours crystallization time. The purity of crystals from controlled cooling crystallization was from 90.1 to 91.7% while for natural cooling was from 88.2 to 89.8%. It was therefore important to have good control in the early stage of crystallization as this would produce crystals with higher purity. Controlled cooling produced slightly higher purity crystals compared to natural cooling mode.

Figure 8: Comparison of product purity for two cooling conditions.

Figures 9 (a-d) show the CSD from two different cooling modes. Comparisons were made on the CSD from the sixth hour onwards as amount of nuclei formed before sixth hour was rather insignificant. At the sixth hour (Fig 9(a)), natural cooling yielded CSD curve which skewed to the right, and controlled cooling yielded balanced a unimodal CSD curve. The median crystal size for controlled cooling is 167 μm ; the median crystal size for natural cooling is 348 μm . This was because uncontrolled cooling occurred during the initial stage of natural cooling (Fig. 6), contributing towards uncontrolled crystal sizes distribution. Through proper control of temperature, the broadness of the CSD curve could be narrowed. From the eighth hour onwards, both modes produced unimodal CSD curve. The median data showed that the controlled cooling produce slightly smaller crystals and narrower CSD curve compared to natural cooling. However, the difference between crystals produced using the two different cooling modes is only marginal at the end of crystallization process.

Figure 9: (a) CSD curve for natural and controlled cooling at the sixth hour. (b) CSD curve for natural and controlled cooling at the eighth hour. (c) CSD curve for natural and controlled cooling at the tenth hour. (d) CSD curve for natural and controlled cooling at the twelfth hour.



4. Conclusion

Three operating temperatures were studied for the crystallization of DHSA. The crystal yield was found to be very sensitive to the operating temperature. The yield dropped substantially from 36% at 24 $^{\circ}\text{C}$ to 7% at 28 $^{\circ}\text{C}$. Higher operating temperature produced crystals of higher purity and bigger size.

Both yield and purity from natural cooling were slightly lower compared to the controlled cooling. Although initially the yield for the natural cooling mode was much lower than the controlled cooling, the quantity of crystals for natural cooling mode increased as time elapsed. At the end of crystallization process, the two different cooling modes produced crystals on similar quality and quantity.

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