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Effect of Cooling Modes on Solvent Crystallization of Palm Oil Based Dihydroxystearic Acid Using Ethanol

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Abstract: In this work, palm based dihydroxystearic acid (DHSA) was produced from epoxidation of oleic acid with performic acid, followed by hydrolysis of the epoxide. The crude DHSA was purified by employing solvent crystallization. Two different crystallization conditions (natural cooling and rapid cooling modes) were studied using ethanol as solvent. Scanning electron microscopy (SEM), gas chromatography (GC) and particle size distribution (PSD) were used to investigate the physical and chemical characteristics of the crystals. The SEM revealed that DHSA forms a sphere-like crystal. After crystallization, purity of the DHSA increased from 69.3 to 86.8-91.4%. It was observed that natural cooling mode yielded a broader distribution and larger particle diameter compared to rapid cooling mode.

Key words: Dihydroxystearic acid, hydroxyl fatty acids, solvent crystallization, scanning electron microscopy, particle size distribution

INTRODUCTION

Personal care industry has shown considerable interest in hydroxyl fatty acid due to its different characteristic compared with ordinary fatty acids (Weber *et al.*, 1995). Hydroxyl fatty acids and its derivatives have been used commercially for the preparation of many kinds of products, i.e. as additives in lubricants, as auxiliaries for the textile and cosmetics industry and as surfactants in detergent products (Dahkle *et al.*, 1995). The main source of hydroxyl fatty acids is castor oil however, oleic acid, which is a low value by-product from the fractionation of palm kernel oil is a potential alternative for the production of hydroxyl fatty acids.

Dihydroxystearic acid was produced from epoxidation of oleic acid with peracetic acid. The epoxide was then hydrolyzed in an aqueous solution resulting 9, 10-dihydroxystearic acid (Roila *et al.*, 1998). The laboratory process of crude DHSA had been successfully scaled-up into pilot plant production. Performic acid was employed to replace peracetic acid to reduce cost, processing time and increase process efficiency (Siwayanam *et al.*, 2004). The presence of hydroxyl and

carboxylic groups in the fatty acid chain provide various reaction sites for the preparation of many useful derivatives. Preliminary study indicated that DHSA can be used as thickener or gelling agents in cosmetics preparation. Functionalities of DHSA in the cosmetics has been described, i.e. the binding agents in compact powder, improving mechanical properties of lipsticks and enhancing the pigment dispersion. For usage in cosmetic application, a non-irritant product is essential. Crude oleic acids normally contain a significant amount of octanoic acid, C8 and decanoic acid, C10. This makes crude DHSA irritant to skin. For this reason, a further step was required to produce non-irritant DHSA, which is via the crystallization process followed by filtration and drying steps.

Crystallization is an important unit operation in the manufacture of high value specialty chemicals. The physical properties of the crystals such as its habit and crystal size distribution, determine the quality of the final product. Usually, large crystals with narrow size distribution result in good filterability. In order to get specified crystal habit and particle size distribution with good reproducibility from one batch to another, optimization of operation conditions such as cooling

mode, stirring effect, seeding or fine dissolution is required.

The aim of this paper was to study the effect of cooling modes in the crystallization process. Ethanol was used as solvent in the crystallization process. Two different cooling conditions were used, i.e. rapid cooling mode (rapid crystallization) and the natural cooling mode (slow crystallization). The results on scanning electron microscopy, gas chromatography and particle size distribution were discussed.

MATERIALS AND METHODS

Experimental procedure: Crude DHSA was melted and kept homogenized for one day to destroy all the crystal memory. Molten DHSA and ethanol were mixed in a beaker at three different ratios, i.e. 1:1, 1:1.5 and 1:2 w/v ratios. These mixtures of samples were then left for 24 h (without stirring). The sample was then filtered through the vacuum system until the filtrate was fully removed. Filter cloth with 25 μm pore size diameter was used to retain the DHSA crystals. The crystals were then put into petri dish and dried in an oven at 50°C for 48 h. The amount of crude DHSA for every experiment is fixed at 150g and only the quantity of solvent varies according to its ratio. Two different crystallization conditions have been examined, which are the slow and rapid crystallization. For slow crystallization, the solution is placed for 24 h in a room without any convective air flow. For rapid crystallization, the solution was cooled for 24 h in freezer, equipped with temperature controller set at 5°C.

Materials: Crude DHSA was prepared in the pilot plant (Siwayanam *et al.*, 2004). Ethanol was purchased from Chemi Industries (Malaya) Sdn. Bhd. Filter cloth made of nylon fabric (25 μm) was provided by Jaya Filter Sdn. Bhd. All other reagents were of analytical grade and were used as received.

Gas chromatography: GC analysis was carried out using Hewlett-Packard HP-6860A plus gas chromatograph (Palo Alto, CA). The samples undergo silylation process before being injected into the gas chromatography equipment. The trimethylsilyl (TMS) derivatives of the samples were separated on a nonpolar column HP-5 (Hewlett-Packard, 30m x 0.25mm x 0.25 μm) with helium as the carrier gas. The oven was programmed to hold at 150°C for 1 min, followed by ramping from 150°C to 290°C at a rate of 10°C/min. The final temperature was held at 290°C for 30 min. The injector and flame ionization detector were set at 300°C (Roila *et al.*, 2001).

Scanning electron microscopy: Crystal morphology was observed using scanning electron microscopy, using the Quanta 400 and EDAX (GENESIS 7000). The specimen

were mounted on a metal stub with double-sided adhesive tape and coated under vacuum with gold in an argon atmosphere prior to observation. The crystals were photomicrograph at magnification of 500, 1000, 1500 and 2000 times.

Particle size distribution: Wet dispersion laser diffraction measurements were performed with Malvern Instruments Mastersizer 2000 and Hydro 2000S particle size analyzer (Malvern, UK). Particle size measurement over the range 0.02-2000 μm was used. The Mie-Scattering model was used for the measurement of the diffraction pattern. The principle is based on simultaneous multi angle detection of scattered light. The scattering behavior is strongly dependent on the particle size. Water acts as the dispersant with 1.330 Reflective Index (RI) and for DHSA, the RI was set at 1.458. A small amount of DHSA crystals was added into water. Then, it was introduced into the dispersion module until an adequate obscuration level was obtained. The particle size distributions were measured three times for each sample.

RESULTS AND DISCUSSION

Crystal morphology: Figure 1 shows DHSA crystals under two different cooling conditions. It is clear that both conditions produced a sphere-like crystal. The results also showed that the size of crystals produced from rapid crystallization is smaller compared to crystals from slow crystallization. It can be concluded that increasing the rate of cooling will decrease the crystal size, due to incomplete growth of a larger number of small crystals. In other words, lower temperature caused higher supersaturation leading to increased nucleation and forming many small crystals.

Particle size distribution analysis: In the crystallization of organic fine chemicals, there is an increasing demand for control of the product particle size distribution. The particle size distribution has an influence on the downstream filtration and washing and may also be a key parameter in handling of the powder. For DHSA, particle size distribution was obtained by sampling weight quantities of particles that were pre-sorted by size.

A typical particle size distribution is shown in Fig. 2. For slow crystallization, as the amount of solvent increases, the width of distribution moved towards the smaller particle size. The median particle size obtained from slow crystallization are 407 μm for 1:1 ratio, 329 μm for 1:1.5 ratio and 296 μm for 1:2 ratio respectively. This indicated that at higher solvent usage, smaller particle was formed. However, for rapid crystallization, the situation was reversed. The width of distribution moved towards the larger particle size. The median particle size data for

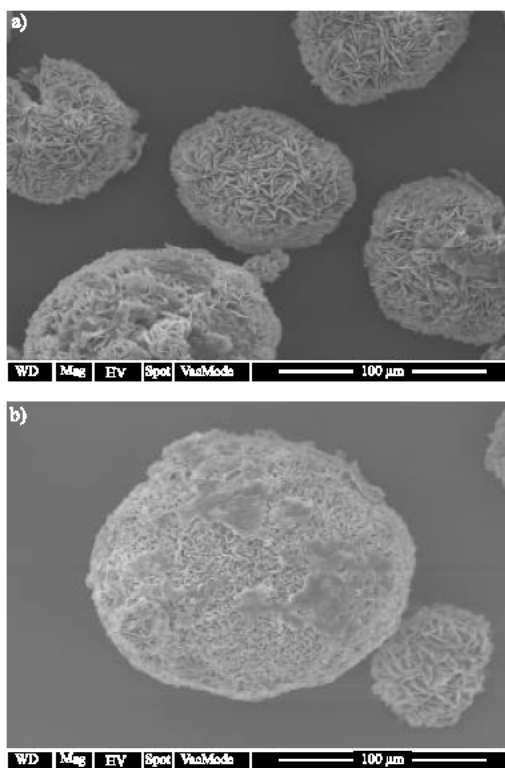


Fig. 1: SEM of crystal products obtained from the crystallization of DHSA at two different conditions: (a) rapid crystallization and (b) slow crystallization at 1000 times magnification

rapid crystallization are 202 µm for 1:1 ratio, 213 µm for 1:1.5 ratio and 252 µm for 1:2 ratio, respectively. The main reason was due to the occurrence of agglomeration among the crystals. A fast cooling rate during the early stage of cooling modes produced a large number of small nuclei. At 1:1 ratio, we noted that rapid crystallization produced much smaller crystal compared to slow crystallization. As the solvent percentage increases, the distribution curve for rapid crystallization moving towards the larger particle and the broadness of the distribution was also increased. This phenomenon denotes the agglomeration process. As noted before from the slow crystallization curve, at higher solvent percentage, the DHSA crystals become smaller. Agglomeration degree depended on the particle size. Generally, particles in smaller size fractions create higher agglomeration degree. The higher the usage of solvent, the smaller will be the particle size and the tendency to create agglomeration was also increased. Rapid crystallization creates much smaller particle size compared to slow crystallization and therefore the tendency of agglomeration is greater. Natural cooling mode creates a stable distribution in terms of the curve

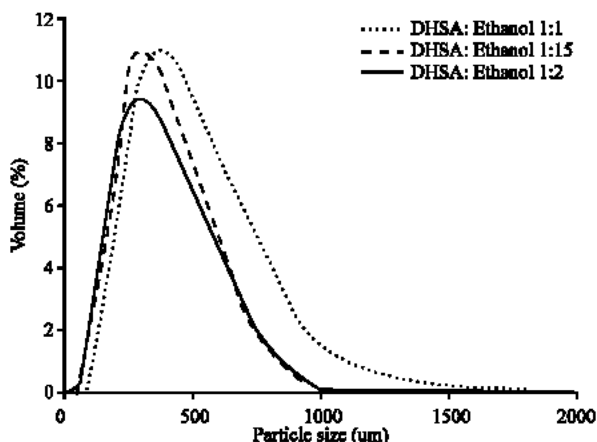


Fig. 2: Particle size distribution of 3 different DHSA:Ethanol ratios for rapid crystallization

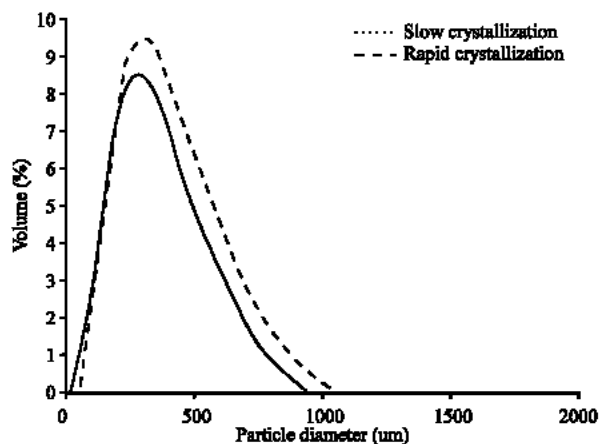


Fig. 3: Comparison of yield between slow and rapid crystallization

broadness where it shows only a slight difference between the three ratios.

Yield and gas chromatography analysis on purified DHSA using ethanol as a solvent: Figure 3 shows the quantity of DHSA crystals produced after 24 h of crystallization, for both cooling condition. The higher the amount of solvent used, the lesser the purified DHSA crystals are obtained. The yield of purified DHSA is calculated by dividing the amount of purified DHSA with amount of crude DHSA. The values were determined in terms of percentage. The yield of DHSA crystals for slow crystallization reduced from 28.2 to 16.8% and for rapid crystallization, the yield reduce from 41.6 to 33.9%, when the solvent ratio increased from 1:1 to 1:2 ratios. This outcome closely related to the function of solvent, which is used to remove impurities from the crude DHSA. The higher the amount of solvent used, the purer will be the

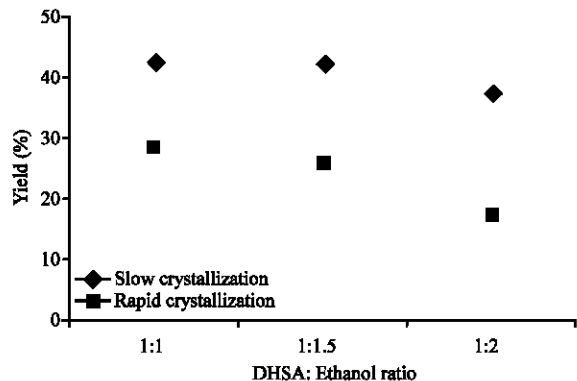


Fig. 4: Comparison of purity between slow and rapid crystallization

product. The purity resulted for slow crystallization ranged from 89.9 to 91.4% and for rapid crystallization, it ranges from 86.8 to 91.3%, for 1:1 to 1:2 ratios respectively. However, it was noticed that at 1:1 and 1:1.5 ratios, the purity of DHSA for rapid crystallization (Fig. 3) was slightly lower compared to slow crystallization. At 1:2 ratios, the values were nearly the same for both cooling modes.

Figure 4 shows the purity of the product from rapid crystallization increased notably with increasing solvent and for slow crystallization, the DHSA purity increased slightly with the amount of solvent used. For a fast cooling rate, many nuclei were formed early in the crystallization process and these nuclei remained throughout the crystallization process. A slow rate of cooling led to formation of regular fat crystals that were easily filtered, producing a consistent product yield and quality. On the other hand, fast cooling rate created a large number of small nuclei and tend to develop higher agglomeration degree. The fast cooling condition can lead to liquid entrainment during the filtration process. Liquid entrainment with the solid fraction after filtration influences the physical and chemical qualities of the desired fraction in laboratory and commercial processes. This liquid-like component, i.e. impurities and mother liquor adsorbed within the crystals or remains between individual crystals during filtration process. DHSA crystals having uniformed size and shape will ease the filtration process and will minimize the liquid entrainment between crystals. Crystal slurry with wide distribution sizes creates higher tendency for liquid to trap between crystals.

CONCLUSION

Solvent crystallization of palm-based DHSA was successfully carried out. Two different cooling modes

were explored, which are the rapid cooling condition (rapid crystallization) and slow crystallization via the natural cooling mode. The amount of solvent played an important role in producing good quality crystals. Generally, increasing the amount of solvent increases the purity of the product, but on the other hand, it reduces the yield of the product. This reduction was due to the removal of more impurities with excessive amount of solvent. The GC analysis that revealed the purity results had supported these findings. Different crystallization conditions also have affected the particle size distribution of the product. Slow crystallization creates a broader distribution curve and larger particle diameter compared to rapid crystallization. From the scanning electron microscopy results, both conditions have created sphere-like crystals. The experiment conducted had concluded that crystallization of DHSA via the natural cooling mode gives better performance compared to rapid cooling mode, more or less in all aspects.

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