수정진동자를 이용한 유기산의 결정화 측정

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Determination of Fatty Acid Crystallization Using a Quartz Crystal Resonator

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INTRODUCTION

Though the nucleation rate in cooling crystallization is important information for the process operation, its measurement requires special analytical instruments leading to experimental difficulty. The nucleation rate in cooling crystallization is closely related to the shape and size of crystallization products which are key factors determining the product quality.

The quartz crystal oscillator comprised a thin quartz crystal sandwiched between two metal electrodes that establishes an alternating electric field across the crystal, causing vibrational motion of the crystal at its resonant frequency. This frequency is sensitive to mass changes and fluid property at the interface of the crystal and its electrode [1]. For example, a 9 MHz resonator detects a mass variation of 1.4 ng/Hz from resonant frequency measurement [2]. Because the resonator is so sensitive, it can be utilized to determine a phase change in microscale near the resonator interface without varying the composition of measured solution. The crystal formation and growth in a cooling crystallization has been monitored with the quartz crystal resonator to find the beginning moment of crystallization [3], to determine a metastable zone width, and to measure the hysteresis between the processes of crystallization and dissolution.

Fatty acids have been widely used as functional materials in plastic, fiber, food, surfactant and biochemical industries. The fatty acids are generally yielded from plant produce in the form of mixture of molecularly similar compounds to make purification difficult. Crystallization after molecular distillation gives highly concentrated product [4]. Seeds including lauric acid are widely used in food industries requiring high purity products. Because distillation, one of the most common purification processes, is not enough to obtain highly pure lauric acid, the crystallization has to be applied in the process. The hydrophobic fatty acids are miscible in organic solvents, but they are partially miscible in aqueous solutions. As a result, the fatty acid crystallization in an aqueous solution for purification has a quite different characteristic compared with common homogeneous phase crystallization. When the crystallization process of lauric acid from a mixed aqueous ethanol solution of lauric acid and myristic acid was combined with an extraction process, the purity of the yielded lauric acid was significantly raised [5].

In this study, a simple device using a quartz crystal resonator is utilized to monitor nucleation and crystal growth for the investigation of nucleation in a cooling crystallization process of dilute lauric acid solution. In addition, the crystal shape is measured from the microscopic observation of resonator surface to examine the moment of nucleation and crystal growth. The temperature of the frequency variation is compared with that from the microscopic observation.

RESONANT FREQUENCY

The frequency variation due to the mass load change of the crystal produced on the electrode surface of a quartz crystal resonator is computed from the following equation [6].

$$\Delta f = \frac{-2 f_0^{\,2} \Delta m}{A(\mu_0 \rho_0)^{1/2}} \tag{1}$$

where f is the resonant frequency, m is the mass load, A is the piezoelectrically active area, μ is the elastic constant, ρ is the density, and the subscript 0 denotes the quartz plate. When the monomer is applied on the resonator surface, the sample amount is determined from the frequency decrease.

EXPERIMENTAL

A 5.5 g of lauric acid is dissolved in a 50 mL of *n*-propanol and water mixture (50 vol. %). While the solution is supplied to the measuring cell at a rate of 5 mL/min, the temperature of the solution is lowered at a rate of 1 °C/min. The experimental setup is shown in Figure 1. The flow rate of coolant is adjusted to the control of the solution temperature. The sensor module was placed on top of the oscillation circuit box, and the two conductors of the quartz crystal oscillator were directly connected to the oscillation circuit. When the temperature of the lauric acid solution is stable, the coolant is supplied first at a rate of 7.5 mL/min for the first run. The rate is adjusted for the solution temperature. After about 5 minutes when the resonant frequency has stabilized, the lauric acid solution is introduced at a rate of 5 mL/min. The frequency has been stable after another 5 minutes, and the coolant flows lower the coolant temperature at a rate of 1 °C/min while the solution temperature is kept constant. The resonant frequency of the resonator and the temperatures of the solution and coolant are continuously measured from the beginning and stored in a PC.

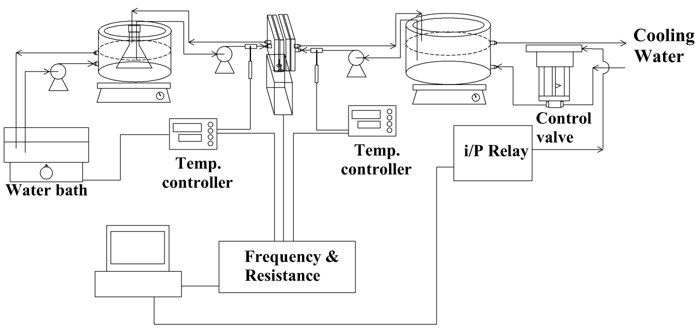

Figure 1. Schematic diagram of experimental setup.

RESULTS AND DISCUSSION

In the first run of the experiment with the lauric acid solution, the variation of resonant frequency along with the coolant temperature is demonstrated in Figure 2. Two apparent slopes of the frequency shift are observed in the figure. When the coolant temperature lowers

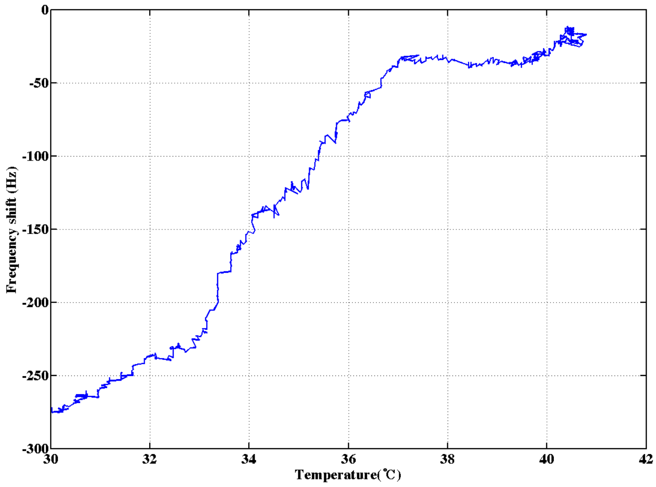

Figure 2. Variation of frequency shift with the lowered coolant temperature indicates the formation of crystal on the resonator surface.

below 37 °C, the frequency drops in a slope until the temperature reaches around 33 °C. Then another decrease begins in a slightly less slope. The frequency is obtained after the deduction of a blank test result, and therefore the effect of temperature variation is eliminated. The first decrease of the frequency indicates the oily nucleation of the lauric acid, which is observed in Figure 3. The photograph of the microscopic observation shows the surface of the quartz crystal resonator covered with oily lauric acid. When the temperature drops further, the bulk lauric acid formulates on the resonator surface as demonstrated in Figure 4.

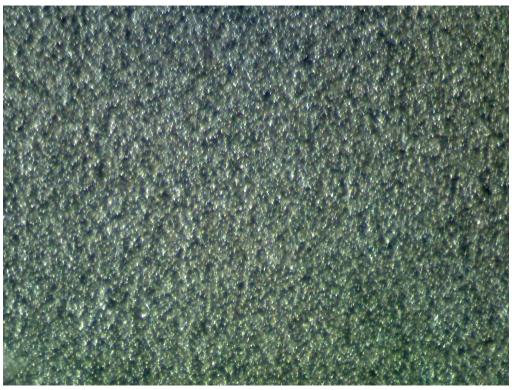

Figure 3. Photograph of the resonator surface coated with oily lauric acid.

The variation of the resonant frequency shows the formation of lauric acid crystal. Though the monitoring of fatty acid crystal is important to control the crystallization for a specific formation of the acid in its shape and purity target, the direct measurement of the crystallization is difficult. The in-line monitoring of the fatty acid crystallization using the quartz crystal resonator is relatively simple and efficient to observe the process.

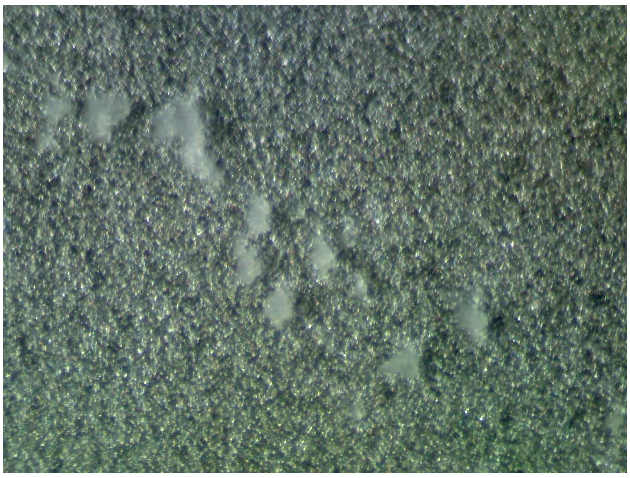

Figure 4. Photograph of the resonator surface with bulk lauric acid.

CONCLUSION

While the lauric acid solution in *n*-propanol and water mixture is cooled, the formation of lauric acid crystal on the surface of a quartz crystal resonator is monitored. The variation of the resonant frequency of the quartz crystal resonator is investigated by comparing with the microscopic observation of the resonator surface. The comparison indicates that the monitoring of the frequency shows when the crystallization begins and when the crystal grows while the solution temperature drops. The utilization of the QCR in this study proves the effectiveness of the QCR monitoring in the crystallization of fatty acid.

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