

Application of solute distribution theory to melt crystallization of fatty acids



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HIGHLIGHTS

- Melt crystallization of fatty acids as biodiesel related mixtures.
- Solute distribution at the solid–liquid (S–L) interface.
- Interfacial solute distribution factor.
- Relationship between the purity of the crystal and the solidification conditions.
- Numerical calculation of the interfacial solute distribution factor.

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ABSTRACT

To study solute distribution at the solid–liquid (S–L) interface during melt crystallization, we examined the applicability of the interfacial solute distribution factor proposed based on a kinetic model involving both mass and heat balances at the interface. The factor derived from the model was compared with the experimental results obtained by employing a binary melt with the different species and concentrations of fatty acids as biodiesel related mixtures. As a result, we were able to reveal the empirical relation between the purity of the crystal and the solidification conditions of the melt. Based on the model, we also numerically calculated the transient changes in the interfacial solute distribution factor as well as the temperature of the S–L interface in the solidification process of the melt. The minimization of the factor was confirmed when the melt was supercooled at the S–L interface after starting solidification.

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1. Introduction

The Neumann–Stefan problem, i.e. movement of a solid–liquid (S–L) interface during the solidification process of a pure liquid, has received great interest by a number of researchers (such as Bird et al. (2002)). This problem, however, focuses only on the heat transfer phenomenon with phase transitions of a single-component system. On the other hand, solidification of a multi-component liquid, known as melt crystallization, is one of the energy-efficient separation technologies utilized in industrial processes for the purification of organic and metallic materials. The industrial process of melt crystallization requires optimized

operating conditions to obtain high purity solids or crystals, as the purity of the solid layer is determined by the kinetics of solute distribution at the S–L interface.

In previous studies on melt crystallization, several kinetic models were proposed to describe the distribution at the S–L interface (Tiller et al., 1953; Cheng and Pigford, 1971; Edie and Kirwan, 1973; Myerson and Kirwan, 1977; Burton et al., 1987). Matsuoka and Garside (1991, 1993) first identified the significance of heat and mass transfers for crystal growth. The non-isothermal effective distribution factor was expressed as a function of the dimensionless growth rate. Chianese et al. (Chianese and Santilli, 1998; Parisi and Chianese, 2001) developed a mathematical model to predict the effective growth rate of solid layers in several organic systems. With regard to the impurity distribution in the solid layer, Slaughter and Doherty (1995) reported a thermodynamic approach applicable to an ideal system without

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employing non-equilibrium factors. Guardani et al. (2001) proposed an empirical model to describe the distribution coefficient in actual industrial processes of melt crystallization, which was performed using a falling film method. Recently, Jiang et al. (2012) developed a model by including impurity distribution in the falling film method. In addition, Jiang et al. (2014) reviewed the progress of recent researches on modeling the crystal growth and the distribution of impurities in melt crystallization.

However, as far as the authors have investigated, the conclusive relationship between the purity of the solid and the operating conditions has not yet been revealed. This is because solute distribution at the S–L interface under unsteady and non-equilibrium conditions has not yet been sufficiently understood. Under equilibrium or quasi-equilibrium conditions, the purity of the solid obtained through melt crystallization can easily be predicted from a phase diagram. However, S–L phase transitions under non-equilibrium conditions result in an unsteady distribution of solvents or impurities in the solidified crystal. In a practical case, the purity of the solid decreases upon inclusion of solvents or impurities at the S–L interface. To predict the purity profile in the solid layer during melt crystallization, the solute concentration and the temperature of the growing solid layer must be determined. The solute distribution at the S–L interface, which causes mass transfer of solute from the melt to solid layer, is essentially governed by the mass balance at the S–L interface. On the other hand, the growth rate of the formed solid layer is also affected by the heat balance at the S–L interface based on the heat transfer rate from the solid to liquid phases. In addition, since the S–L interface moves unsteadily at the growth rate of the solid layer, the kinetics of heat and mass transfers are also influenced by the flow structure in the liquid phase. Therefore, to analytically solve the solute distribution problem of a multi-component melt, we need to simultaneously determine four unknown physical variables defined at the S–L moving interface, i.e., temperature, growth rate of the solid layer, solute concentration in the liquid, and solute concentration in the solid.

To calculate mass transfer at the S–L interface under non-equilibrium conditions, it is essential to express the solute distribution coefficient as the ratio of solute concentration in the liquid to that of the solid. Because the melt solidifies at the S–L interface, the interfacial solute distribution coefficient can be expressed as a function of the physical variables defined at the S–L interface. According to “the local lever rule at the S–L interface,” based on the concept of a constitutional supercooling zone (Tiller et al., 1953), we proposed a novel model for solute distribution at the S–L interface (Fukui and Maeda, 1998). Based on this model, we calculated the purity profile of the solid layer by direct numerical simulation (Fukui and Maeda, 1998, 2002a). As a result, we suggested a fundamental relationship between solute distribution and the growth rate of the solid layer (Fukui and Maeda, 2002b). Moreover, we confirmed the validity and applicability of the proposed model to engineering processes (Fukui et al., 2013).

In this study, we propose a simple and convenient model to express the unsteady distribution of solute in the solid layer during melt crystallization. The solute distribution factor at the S–L interface was determined by applying the model equation to the experimental results obtained by employing three different species of binary mixtures of fatty acids, which have been used as raw materials of biodiesel fuel. Then, we discuss the effect of the operating conditions of the crystallization apparatus on both the solid purity and growth rate of the solid layer.

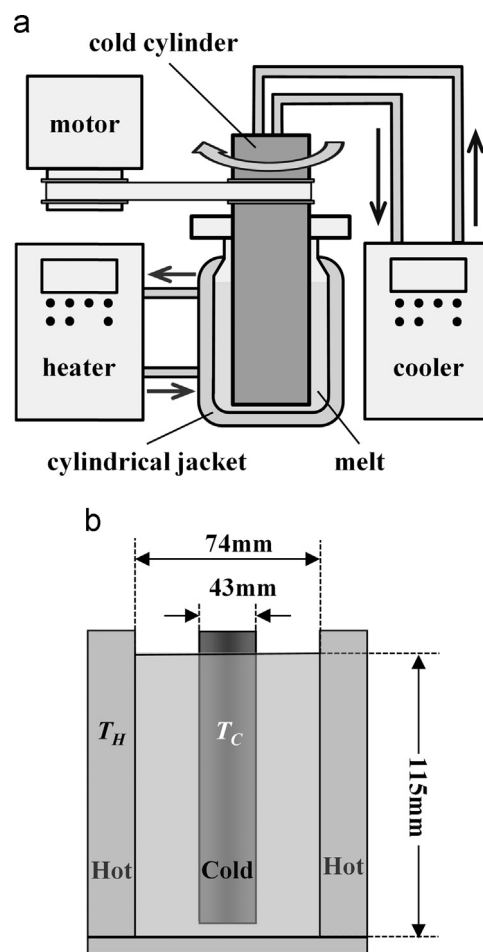


Fig. 1. Schematic images of (a) experimental apparatus used for melt crystallization and (b) crystallizer.

2. Material and methods

2.1. Experimental

In this study, we examined a binary melt containing an unsaturated triglyceride and saturated fatty acid. We used triolein as the unsaturated triglyceride and myristic, stearic or palmitic acids as the saturated fatty acid. The GR grade reagents were purchased from Kanto Chemical Co. Fig. 1 shows the experimental apparatus used for melt crystallization in this study. A cold cylinder with the diameter of 43 mm was set at the center of a cylindrical jacket with the inner diameter of 74 mm and the height of 115 mm. The melt, which was initially kept at 338 K, was put in the annular space between the cold cylinder and the jacket. To fix the flow conditions in the space, the rotation rate of the cold cylinder was kept constant in the range of 100–400 rpm throughout melt crystallization. Then, we initiated melt crystallization by gradually cooling the cold cylinder to 278 K at a constant cooling rate, R_c , of 0.17–1.0 K/min by circulating cold water inside the cylinder. The temperature of the jacket was kept constant at 338 K, which was above the melting point of the binary melt, by circulating hot water outside the jacket. To determine the growth rate of the solid layer, the transient change in the size of the solid layer was observed using a digital camera at a certain time interval. At the end of each run, both the solute concentration and weight of the solid layer were measured. The experimental conditions are summarized in Table 1.

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