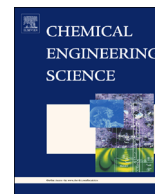




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Solvent-aided layer crystallization—Case study glycerol–water

F.J. Eisenbart*, J. Ulrich

Martin-Luther-Universität Halle-Wittenberg, Zentrum für Ingenieurwissenschaften, Thermische Verfahrenstechnik, D-06099 Halle, Germany

HIGHLIGHTS

- New concept for the separation of high-viscous melts.
- Use of assisting agent to reduce viscosity.
- Successful purification of glycerol from water.
- Reduction of water content by an order of magnitude in one crystallization step.

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ABSTRACT

Solid-layer melt crystallization with an additional assisting liquid medium, just like an extraction solvent, is introduced. A case study of the purification of glycerol from mixtures containing 1–10 wt% water and the use of 1-butanol as additional solvent assisting to control crystallization kinetics is presented. Cold finger experiments were carried out. It was found that in regular melt crystallization without the use of 1-butanol, water concentration could be reduced to 30–80 wt% in comparison to the residual melt at growth rates between 4×10^{-8} and 1.4×10^{-7} m/s, with lower growth rates resulting in lower water concentrations. No post-treatment like sweating or washing was applied. The dependence between purification success and growth rate could not be changed by initial water content or duration of the experiment and only little by agitation of the melt. The use of 1-butanol allowed an improvement of the process in terms of higher product purities and higher growth rates. Distribution coefficients improved by a factor of 2–4 without a loss in the growth rate or growth rates could be increased by a factor 5 without harming the separation quality. The influence of 1-butanol on the crystallization in comparison to that of water is further investigated. An understanding of how to use additional assisting solvents to control crystallization kinetics and to improve the separation is interesting for the purification of other components, especially high-viscous ones such as tocopherols or phytosterols as well.

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1. Introduction

Melt layer crystallization is a thermal separation process with which high product purities can be achieved after few, in some cases even after one process step (Ulrich and Glade, 2003). It is conducted by bringing a liquid mixture, the crude melt, including the desired substance and at least one impurity in contact with a cooled surface, so that the substance will crystallize as a solid layer attached to said cooled surface. Most known organic mixtures have a eutectic phase diagram (Matsuoka, 1977) allowing the growth of almost pure crystals from the mixture. Still, the purity of the crystal layer as a whole, thus the success of the purification process, can be diminished e.g. by inclusion of impure melt

(Wintermantel and Kast, 1973a). This process is controlled by kinetic aspects of crystallization including the transport of the crystallizing substance from the bulk of the melt into the vicinity of the crystal front and the transport of the impurity out of the vicinity of the crystal front (Ulrich and Bülow, 2002). These mass transfer processes have to be fast in comparison to crystal growth in order to achieve a high product purity (Wintermantel, 1986; Wintermantel and Kast, 1973b). This is favored by a high diffusivity and convection. As diffusivity is reciprocal to viscosity (Einstein, 1905) and the possibility of convection is also lower in high-viscous liquids, a high viscosity of the melt usually results in both lower growth rates and poorer separation. Melts with viscosities of more than 0.1 Pa s are, up to now, generally not considered processable in layer crystallization (Ulrich and Nordhoff, 2006). But as there are some products such as phytosterols, tocopherols and glycerol that form high viscous crude melts which are difficult or expensive to separate by other means like e.g. extraction or

* Corresponding author. Tel.: +49 345 55 28 404; fax: +49 345 55 27 358.
 E-mail address: felix.eisenbart@iw.uni-halle.de (F.J. Eisenbart).

distillation, a concept that allows a layer crystallization to obtain these compounds in high purities is highly interesting.

The basic idea of solvent-aided layer crystallization is the use of an additional assisting agent that is added to the melt in sufficiently high amounts to decrease the viscosity in order to change the crystallization kinetics in a favorable way. The additional compound may have multiple positive or negative effects on the crystallization process besides its influence on the viscosity. It is, therefore, important to experimentally determine for each system whether or not a certain solvent is suitable for the task and what concentration and other process parameters are to be chosen. Being an assisting agent, the solvent should be recyclable in the overall process, just like in an extraction process.

In this first case study, a binary system of glycerol as main component and water as impurity was chosen. This mixture is a good example for a high viscous liquid which is difficult to separate. Furthermore, it is a system of commercial interest. A binary phase diagram of the system glycerol–water was measured by Lane (1925). The viscosity of pure glycerol is 1.56 Pa s at its solid–liquid equilibrium temperature of 290 K and 12 Pa s at 273 K (Segur and Oberstar, 1951). With increasing water content, the solid–liquid equilibrium temperature decreases almost linearly to 227 K for a water content of 33.3 wt% (Lane, 1925). For water contents up to 10 wt%, the equilibrium viscosity, that is the viscosity at the solid–liquid equilibrium temperature, shows the behavior depicted in Fig. 1 based on the experimental data provided by Lane (1925) and Segur and Oberstar (1951). When water is added, the equilibrium viscosity passes through a maximum and does not decrease far below the value for pure glycerol. It stays well above the limit of 0.1 Pa s mentioned above.

Crude glycerol is abundantly available as a by-product of the biodiesel production (Almeida et al., 2012). Pure glycerol, on the other hand, has a wide range of applications, e.g. in food, cosmetics, pharmaceuticals or as starting material for the production of other chemicals or fuels (Johnson and Taconi, 2007). The crude glycerol obtained by biodiesel production usually contains 30–60 wt% glycerol (Hájek and Skopal, 2010). The most important impurities are, depending on the biodiesel plant, fatty acids, organic and inorganic salts, methanol or ethanol, and water. Different methods for the removal of non-aqueous impurities and the production of glycerol mixtures with 80–95 wt% glycerol have been proposed (Carmona et al., 2009a, 2009b; Chiu et al., 2005; Hájek and Skopal, 2010; Hazimah et al., 2003; Kongjao et al., 2010; Ooi et al., 2001; Potthast et al., 2010; Stromquist and Reents, 1951; Wiesen et al., 2014), but for the removal of water and the achievement of high purities, an alternative to vacuum distillation is missing up to now. Distilling parameters are, however, rather unfavorable. One finds e.g. 393–399 K at 4–40 Pa (Yong et al., 2001) or 413–433 K at 10–300 Pa (Hazimah et al., 2003) described

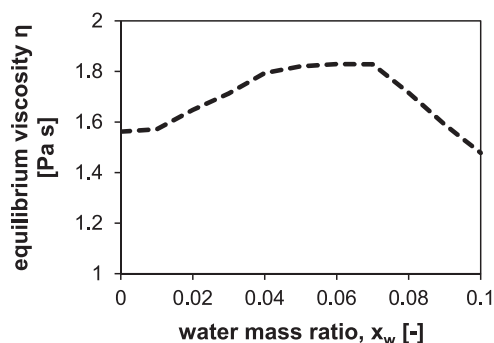


Fig. 1. Viscosity of binary glycerol–water mixtures at their respective solid–liquid equilibrium points. Calculated from phase diagram in Lane (1925) and viscosity tables in Segur and Oberstar (1951).

in the literature. In addition, multiple steps are often necessary. Using layer crystallization for this last purification step would, therefore, be an interesting alternative.

Use of an additional solvent to allow efficient suspension crystallization of glycerol has been proposed by Hass (1941) and Hass and Patterson (1941). They screened different solvents for their ability to allow faster growth of the crystals in suspension crystallization. Liquid ammonia and 1-butanol were found to be most suitable for this purpose. However, they did not provide any quantitative data, neither on growth rates nor on purification success, nor did they give any temperature levels, compositions or undercooling so that evaluation or comparison of their results is virtually impossible. Their process drew little interest and there was no attempt to apply the concept on layer crystallization. The hint to 1-butanol is, however, important. 1-butanol is a relatively poor solvent for glycerol in contrast to the impurity investigated in this study, water, which is miscible with glycerol in every ratio over a wide range of temperatures. Hass and Patterson (1941) reasoned that 1-butanol could be added to glycerol in amounts high enough to strongly reduce the viscosity without reducing the vapor pressure of the crystallizing substance to much. Furthermore, it can be expected to be easy to remove any traces of 1-butanol from glycerol. In contrast to this, contamination of the product might become a major problem in case of a solvent with better miscibility. These were the reasons to choose 1-butanol as solvent in this study. However, its applicability cannot be predicted theoretically but has to be shown by experiment.

2. Experimental

2.1. Seed crystal production

Seed crystals were produced by cooling glycerol samples with liquid nitrogen and subsequently store them at 248 K, packed in a styrofoam box with a wall thickness of approximately 0.1 m. This procedure is necessary because nucleation of glycerol only takes place within the temperature interval from ca. 205 to ca. 230 K with a narrow peak at ca. 212 K (Matz, 1969) while crystal growth only takes place at higher temperatures and the growth rate reaches its maximum at 266 K (Günther et al., 1956). The insulation and low ambient temperature allow the temperature of the glycerol to rise so slowly that the time within the temperature interval in which nucleation takes place is long enough to produce enough stable nuclei. These will then start to grow when the temperature rises further. Gibson and Giauque (Gibson and Giauque, 1923) first reported that glycerol crystals were obtained by warming glycerol very slowly from liquid air temperature to room temperature.

2.2. Seed crystal growth

The growth rates of seed crystals in different binary glycerol–water and glycerol–1-butanol mixtures were determined by putting the mixtures into tubes or flasks with seed crystals at their bottom, or into petri dishes with seed crystals in the centre, and store them at 248 K or 279 K. At these temperatures, no nucleation of glycerol crystals takes place (Matz, 1969). The crystal growth rate can, therefore, be determined by collecting the position of the crystal front after different times after seeding. These measurements were done in situ. The crystals were not fixed to the center of the dish but all experiments in which the seed crystal changed its position were not taken into account. In case of a decrease in growth rate as result of the decreasing glycerol concentration towards the end of an experiment, only the constant growth rate at the beginning of the experiment, when the glycerol

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