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Production of highly dry glycerol by solvent-aided melt layer crystallization

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ABSTRACT

Purification of highly viscous pre-purified glycerol to purities of more than 99.9% was performed by solvent-aided melt layer crystallization. Two different setups were used and suitable assumptions for data evaluation that makes results between the setups comparable are presented. Adding 5–30 wt% of 1-butanol to the melt drastically increased the separation performance of a layer crystallization. Purities of up to 99.95% were reached at growth rates of 10^{-7} m/s, even without post treatments. At higher growth rates or without 1-butanol, layers of lower purity can be grown and then subjected to a sweating-like post treatment, which is effective but does not compensate the influence of solvent or growth rate. Results suggest an effect of migration of liquid inclusions in the crystal layer.

1. Introduction

Attaining glycerol of very high purity from the biodiesel by-product is a complicated process but it is economically justified by the abundance of the raw mixture and the high demand for pure glycerol, e.g. in food and pharmaceutical industry. In some approaches, impurities like fatty acids, esters and catalysts or salts are removed by a series of chemical treatments, extraction and absorption steps before water is removed by means of multi-stage vacuum distillation. In others, a series of three different distillation columns with the glycerol being the middle distillate of the last one allows the separation of most impurities, including ions, by distillation only. Nevertheless, pH-adjustment and an additional bleaching with active carbon is still necessary. Temperatures in this process exceed 180 °C at 10 mbar. While water contents around $x_w = 0.01$ are relatively easy to attain, targets of x_w " 0.01 make the process often very expensive due to the need of an increased number of stages.

For the special task of achieving very high purities from pre-purified feeds, melt layer crystallization is often suitable [1], especially if the mixture is, like most known organic mixtures, of eutectic nature [2] and vapour-liquid-equilibria are somewhat unfavourable. These criteria are met in the present problem, but also the viscosity of the feed close to its freezing point exceeds 0.1 Pa s which has been deemed to be the upper limit of applicability of melt layer crystallization [3]. Solvent-aided melt layer crystallization uses small quantities of a solvent, in this case 1-butanol, to overcome this problem [4,5]. Efficiency of the melt layer crystallization is measured by the ratio of impurity concentrations in product to residuum, called here the distribution coefficient, k, and by the size of equipment necessary for a certain product mass stream. The latter depends on the growth rate, G, and the product loss during the sweating-like post treatment for which the post treatment yield,Y_{PT}, is a measure [5]. Desirable are low values for k while G and Y_{PT} should be high.

2. Materials and methods

2.1. Feed

Glycerol mixtures used in this study were mixed from the product of previous crystallizations, glycerol (Roth, Germany, pH. Eur.), 1-butanol (Roth, synthetic grade) and tab water. The mass ratio of water to glycerol was fixed to $\xi_{wg} = 1/99$ kg (water)/kg (glycerol) and checked by Karl Fischer titration. Butanol was added to mass fractions of $x_b = 0$ to $x_b = 0.3$ in the resulting feed to the layer crystallization.

2.2. Experimental setups

Two different layer crystallization setups were used. The first one is a cold finger setup described in a previous paper [5]. Providing a vertical tube as cold surface and a vertical line of seed crystal attached to the same, it allows horizontal growth of the

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Nomenclature

Latin alphabet

G	crystal growth rate m/s
h	vertical height of crystal layer m
k	distribution coefficient -
m	total deposited mass kg
r	radius, radial coordinate m
T	temperature °C
t	duration of crystal growth s
x	mass fraction -
y	vertical, axial coordinate m
Y	yield -

Greek alphabet

ΔT	Temperature difference K
ξ	weight ratio -
ρ	density kg/m³
τ	time constant s
φ	angular coordinate -

Indices (subscripts)

0	at the cold finger
1	at the end of the experiment
b	1-butanol
B	at the beaker wall
C	crystal
g	glycerol
PT	post treatment
w	water

Indices (superscripts)

*	in equilibrium
Res	residue

crystal layer both around the cold finger and in radial direction. The temperatures of cold finger and beaker are held constant over the course of the experiment, with the beaker temperature being 20 K higher than the cold finger temperature, which means that the temperature at the crystal front is increasing as it moves from the cold finger towards the beaker wall. After the growth step, a sequence of liquid samples is drained from the beaker: First the bulk of the residual melt, then the residual melt that initially adhered to the cold surface but slowly drops off without an increase in temperature from crystallization step, followed by different fractions of the crystal layer as it gradually melts during stepwise heating of cold finger and beaker. This partial melting is considered the post treatment and evaluated as described elsewhere [5].

Additionally to the cold finger experiments, layer crystallization was performed in glasses of 25 mm inner diameter, a cooling jacket with uniform temperature around bottom and sides up to a height of 60 mm, in which the layer grew vertically upwards from a seed layer at the bottom covering the entire cross sectional area. Fig. 1 shows the setup. The liquid level was 50 mm. The thickness, i.e. height, of the crystal layer was recorded over time and the growth rate evaluated as described below.

The cold finger setup works similar to an industrial apparatus for static melt layer crystallization and allows a sweating-like post treatment with restrictions discussed elsewhere [5]. The glass setup allows rapid experimentation and detailed growth rate evaluation, but differs from common industrial procedure in its vertical crystal growth and lack of post treatment. The differences in setup geometry, temperature gradients and, therefore, growth rate gradients, have to be compensated by the data evaluation process described below. If the mean growth rate is evaluated sensibly, the results from the two setups should not only be comparable but provide correlations between separation and growth rate applicable to any equipment geometry and temperature gradients.

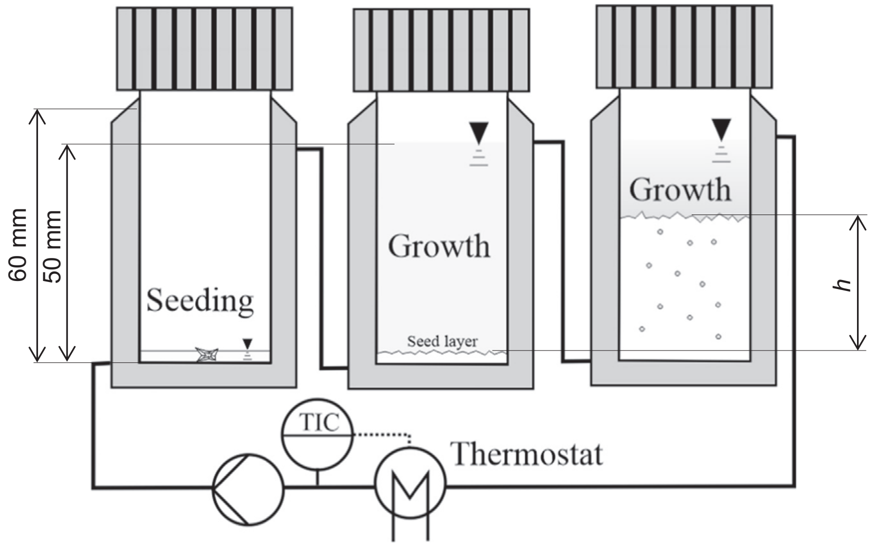

Fig. 1. Sketch of the glass setup.

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